

## Disperse dyes based on 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone

VIJAY H. PATEL, MANISH P. PATEL and RANJAN G. PATEL<sup>#</sup>

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat, India

(Received 10 January, revised 27 July 2002)

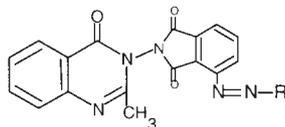
**Abstract:** A series of new heterocyclic disperse dyes has been prepared by subsequent diazotization of 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone and coupling with various mono- and di-*N*-substituted derivatives of aniline. All the disperse dyes were characterized by their percentage yield, melting point, UV-visible spectrum, elemental analysis, infrared spectrum and dyeing performance on nylon 66 and polyester fibres. The percentage dye bath exhaustion on different fibres was found to be reasonably good and acceptable. The dyed fibres showed fair to fairly good to good fastness to light and very good to excellent fastness to washing, rubbing, perspiration and sublimation.

**Keywords:** 3'-aminophthalimido; quinazolinone; synthesis; nylon 66 fibres; polyester fibres; dyeing properties.

### INTRODUCTION

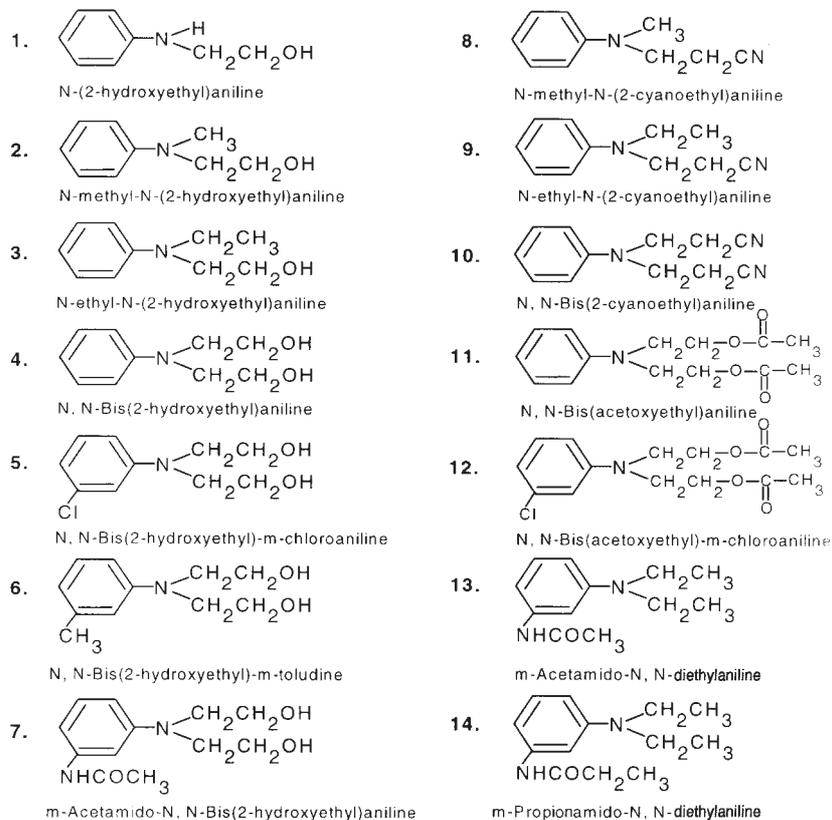
Disperse dyes from amino heterocycles, such as quinoline,<sup>1,2</sup> isoquinoline,<sup>3</sup> cinnoline,<sup>4</sup> phthalazine, quinoxaline<sup>5–7</sup> and quinazoline<sup>8,9</sup> have been reported in the patent literature as being promising disperse dyes. It has been shown that dyes based on the 4-ketoquinazolinone moiety<sup>10,11</sup> possess good fastness properties and high stability. Phthalimide derivatives of 4-ketoquinazolinone have been reported<sup>12</sup> but the synthesis of 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone and disperse dyes based on the same moiety have not been reported so far. In the present paper some disperse dyes based on this heterocyclic moiety are reported.

The substituents and their position were selected so as to increase their auxochromic effect in the final azo structure and so to have a variety of shades. The dyeing performance of these dyes were examined on nylon 66 and polyester fibres. Disperse dyes of the following structure were prepared.

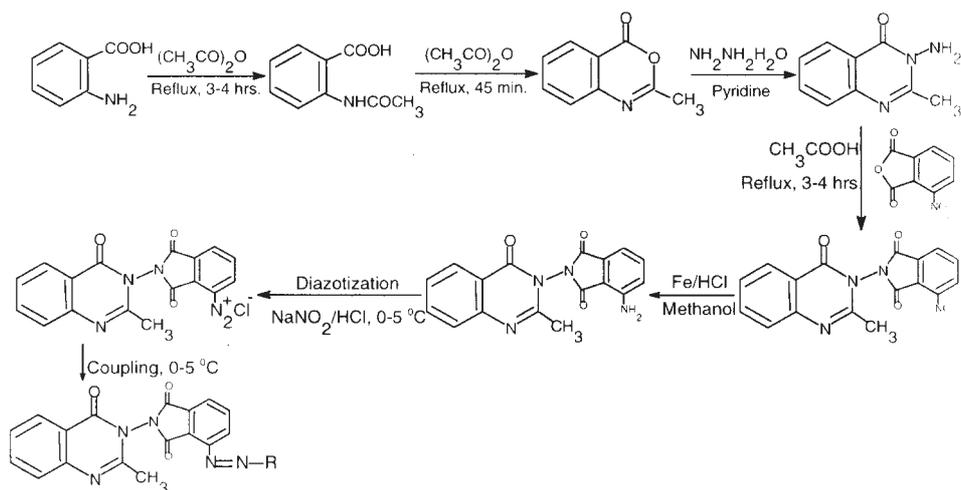


where R= various mono and di-*N*-substituted aniline derivatives, as listed in Chart-I.

<sup>#</sup> To whom all correspondence may be addressed. E-mail: patelvijay\_99@yahoo.com



## Reaction scheme.



R= Various mono &amp; di-N substituted aniline derivatives.

Chart I

## EXPERIMENTAL

All melting points are uncorrected and are expressed in °C. The IR spectra were recorded on a Nicolet Impact – 400 D FT-IR spectrophotometer using the KBr pellets technique. The <sup>1</sup>H-NMR spectra were recorded on a Hitachi R-1500 instrument, using TMS as the internal standard. Chemical shifts are given in δ (ppm). The absorption spectra of the dye solutions in DMF were recorded on a Shimadzu UV 240 instrument. Fastness test to light, sublimation and perspiration was assessed in accordance with AATCC/15/1985. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC/88/1988, and the wash fastness test in accordance with IS: 765-1979.

*Preparation of 3-amino-2-methyl-4(3H)-quinazolinone*

The title compound was prepared following a sequence of reactions according to a procedure described in the literature.<sup>13-16</sup> Yield 80%, m.p. 143 °C, IR (KBr): 3496br cm<sup>-1</sup> (–NH stretching of –NH<sub>2</sub>), 1696s cm<sup>-1</sup> (N–C=O) of quinazolinone and 1310 cm<sup>-1</sup> (C–H stretching of aromatic methyl). Mol. formula: C<sub>9</sub>H<sub>9</sub>N<sub>3</sub>O. Found: %C: 68.61, %H: 5.34, %N: 15.57. Calcd.: %C: 68.97, %H: 5.75, %N: 16.09. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.28 to 8.29 ppm (4H, *m*, aromatic proton), δ 4.94 ppm (2H, *s*, aromatic amine) and δ 2.12 to 2.70 ppm (3H, *s*, aromatic methyl).

*Preparation of 2-methyl-3-[3'-nitrothalamido]-4(3H)-quinazolinone*

The title compound was prepared according to a procedure described in the literature.<sup>12</sup> Yield 74 %, m.p. 194–5 °C, IR (KBr): 1530 cm<sup>-1</sup> and 1360 cm<sup>-1</sup> (–N=O stretching of aromatic nitro), 1696s cm<sup>-1</sup> (N–C=O) of quinazolinone and 1310 cm<sup>-1</sup> (C–H stretching of aromatic methyl). Mol. formula: C<sub>17</sub>H<sub>10</sub>N<sub>4</sub>O<sub>5</sub>. Found: %C: 57.92, %H: 2.44, %N: 15.47. Calcd.: %C: 58.29, %H: 2.86, %N: 16.00. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.27 to 8.26 ppm (7H, *m*, aromatic proton) and δ 2.52 ppm (3H, *s*, aromatic methyl).

*Preparation of 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone*

2-Methyl-3-[3'-nitrothalamido]-4(3H)-quinazolinone (1.75 g, 0.005 mol), methanol (10 ml) and concentrated hydrochloric acid (5 ml) were charged into a 250 ml round bottom flask and heated in a water bath at reflux temperature. Iron powder (1.0 g, 0.018 mol) was added pinch by pinch during one hour with continuous stirring. Stirring was continued under the same reaction conditions for two hours. The reaction mixture was made alkaline with ammonia (50 %) and filtered hot. The filtrate was allowed to cool in an ice-bath. The solid that separated was filtered and crystallized from methanol to give a fine dark brown powder. Yield 62 %, m.p. 212 – 215 °C, IR (KBr): 3410br cm<sup>-1</sup> (–NH stretching, of –NH<sub>2</sub>), 1696s cm<sup>-1</sup> (N–C=O) of quinazolinone and 1310 cm<sup>-1</sup> (C–H stretching of aromatic methyl). Mol. formula: C<sub>17</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>. Found: %C: 63.19, %H: 3.60, %N: 17.24. Calcd.: %C: 63.75, %H: 3.75, %N: 17.75. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ 7.27 to 8.26 ppm (7H, *m*, aromatic proton), δ 3.97 ppm (2H, *s*, aromatic amine) and δ 2.52 ppm (3H, *s*, aromatic methyl).

*Diazotization of 2-methyl-3-[3'-aminophthalimido]-4(3H)-quinazolinone*

Diazotization of the title compound was carried out by the usual method.<sup>17</sup>

*Coupling of the diazo solution with N-(2-hydroxyethyl)aniline (Formation of D<sub>1</sub>)*

N-(2-Hydroxyethyl)aniline (0.37 g, 0.0027 mol) was dissolved in hydrochloric acid (10 % w/v). The solution was diluted with water (6 ml) and cooled to 0–5 °C. To this well stirred solution, a freshly prepared diazo solution at 0–5 °C was added dropwise in about 45 min, whereby the temperature was maintained below 5 °C. Stirring was continued for 24 h at 0–5 °C maintaining the pH in the range 5.0 to 6.0 by the addition of the required amount of an ice-cold solution of sodium carbonate (10 % w/v). The product was filtered, washed several times with water and dried at 40 °C. The brown solid thus obtained was dissolved in a minimum amount of dimethylformamide and precipitated by the addition of chloroform. Yield 75 %, m.p. 198–199 °C, IR (KBr): 3453br cm<sup>-1</sup> (–NH stretching), 1696s cm<sup>-1</sup> (N–C=O) of quinazolinone, 1310 cm<sup>-1</sup> (C–H stretching of aromatic methyl) and 1559s cm<sup>-1</sup> (–N=N– stretching of azo group). Mol. formula: C<sub>25</sub>H<sub>20</sub>N<sub>6</sub>O<sub>4</sub>. Found: %C: 63.72, %H: 3.87, %N: 17.44. Calcd.: %C: 64.10, %H: 4.27, %N: 17.95.

TABLE I. Characterization data and percentage exhaustion of novel 2-methyl-3-[3'-aminophthalimido]-4(3*H*)-quinazolinone disperse dyes

Dye	Coupling component R	Mol. formula	Mol. wt g/mol	Yield %	M.p.* °C	$\lambda_{\max}$ /nm (log $\epsilon$ )	%Found (% Calcd.)			% Exhaustion	
							C	H	N	N*	P*
D <sub>1</sub>	<i>N</i> -(2-hydroxyethyl)-aniline	C <sub>25</sub> H <sub>20</sub> N <sub>6</sub> O <sub>4</sub>	468	75	198–9	460 (4.30)	63.72 (64.10)	3.87 (4.27)	17.44 (17.95)	76	72
D <sub>2</sub>	<i>N</i> -(2-hydroxyethyl)-aniline	C <sub>26</sub> H <sub>22</sub> N <sub>6</sub> O <sub>4</sub>	482	72	185–8	465 (4.38)	64.35 (64.73)	4.15 (4.56)	16.94 (17.43)	70	68
D <sub>3</sub>	<i>N</i> -ethyl- <i>N</i> -(2-hydroxyethyl)-aniline	C <sub>27</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub>	496	80	162–5	468 (4.22)	64.94 (65.32)	4.47 (4.84)	16.42 (16.94)	79	74
D <sub>4</sub>	<i>N, N</i> -bis(2-hydroxyethyl)-aniline	C <sub>27</sub> H <sub>24</sub> N <sub>6</sub> O <sub>5</sub>	512	77	172–5	471 (4.15)	62.92 (63.28)	4.29 (4.69)	15.87 (16.41)	71	69
D <sub>5</sub>	<i>N, N</i> -bis(2-hydroxyethyl)- <i>m</i> -chloroaniline	C <sub>27</sub> H <sub>23</sub> N <sub>6</sub> O <sub>5</sub> Cl	546.5	84	183–5	465 (4.45)	58.89 (59.29)	3.85 (4.21)	14.86 (15.37)	68	65
D <sub>6</sub>	<i>N, N</i> -bis(2-hydroxyethyl)- <i>m</i> -toluidine	C <sub>28</sub> H <sub>26</sub> N <sub>6</sub> O <sub>5</sub>	526	75	200–2	475 (4.32)	63.49 (63.88)	4.53 (4.94)	15.47 (15.97)	78	73
D <sub>7</sub>	<i>m</i> -acetamido- <i>N, N</i> -bis(2-hydroxyethyl)-aniline	C <sub>29</sub> H <sub>27</sub> N <sub>7</sub> O <sub>6</sub>	569	72	160–2	478 (4.15)	60.75 (61.16)	4.32 (4.75)	16.68 (17.22)	74	71
D <sub>8</sub>	<i>N</i> -methyl- <i>N</i> -(2-cyanoethyl)-aniline	C <sub>27</sub> H <sub>21</sub> N <sub>7</sub> O <sub>3</sub>	491	80	190–2	482 (4.27)	65.60 (65.99)	3.89 (4.28)	19.44 (19.96)	73	69
D <sub>9</sub>	<i>N</i> -ethyl- <i>N</i> -(2-cyanoethyl)-aniline	C <sub>28</sub> H <sub>23</sub> N <sub>7</sub> O <sub>3</sub>	505	76	195–8	486 (4.21)	66.19 (66.53)	4.14 (4.55)	18.91 (19.41)	79	74
D <sub>10</sub>	<i>N, N</i> -bis(2-cyanoethyl)-aniline	C <sub>29</sub> H <sub>22</sub> N <sub>8</sub> O <sub>3</sub>	530	82	189–90	490 (4.23)	65.29 (65.66)	3.74 (4.15)	20.59 (21.13)	70	66
D <sub>11</sub>	<i>N, N</i> -bis(2-acetoxyethyl)-aniline	C <sub>31</sub> H <sub>28</sub> N <sub>6</sub> O <sub>7</sub>	596	80	182–5	510 (4.32)	62.09 (62.42)	4.29 (4.70)	13.54 (14.09)	80	78
D <sub>12</sub>	<i>N, N</i> -bis(2-acetoxyethyl)- <i>m</i> -chloroaniline	C <sub>31</sub> H <sub>27</sub> N <sub>6</sub> O <sub>7</sub> Cl	630.5	72	190–2	505 (4.30)	58.62 (59.00)	3.94 (4.28)	12.82 (13.32)	85	81
D <sub>13</sub>	<i>m</i> -acetamido- <i>N, N</i> -diethylaniline	C <sub>29</sub> H <sub>27</sub> N <sub>7</sub> O <sub>4</sub>	537	75	185–8	450 (4.15)	64.43 (64.80)	4.63 (5.03)	17.77 (18.25)	73	70
D <sub>14</sub>	<i>m</i> -propionamido- <i>N, N</i> -diethylaniline	C <sub>30</sub> H <sub>29</sub> N <sub>7</sub> O <sub>4</sub>	551	70	180–2	458 (4.20)	64.97 (65.34)	4.85 (5.26)	17.31 (17.79)	70	67

\*All the melting points are uncorrected,  $\lambda_{\max}$  in DMF, N\* – nylon; P\* – polyester;

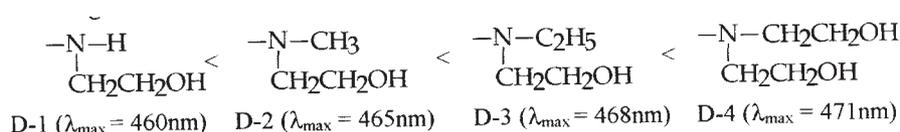
## RESULTS AND DISCUSSION

Heterocyclic compounds of 2-methyl-3-[3'-aminophthalimido]-4(3*H*)-quinazolinone were prepared by the condensation of 3-amino-2-methyl-4(3*H*)-quinazolinone with 3-nitrophthalic anhydride followed by reduction with Fe/HCl in methanol.

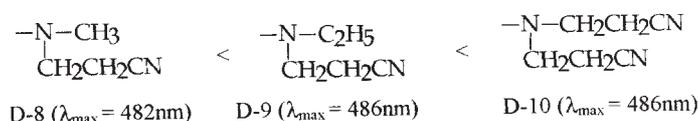
A series of disperse dyes (D<sub>1</sub> to D<sub>14</sub>) was prepared by diazotization of 2-methyl-3-[3'-aminophthalimido]-4(3*H*)-quinazolinone and coupling with various couplers, as listed in Chart I. Diazotization was carried out by the usual procedure using sodium nitrite and hydrochloric acid and the coupling was done in a moderately acidic medium at 0–5 °C. The characterization data, absorption maxima ( $\lambda_{\max}$ ) and logarithm of molar extinction coefficient ( $\log \epsilon$ ) of the 2-methyl-3-[3'-aminophthalimido]-4(3*H*)-quinazolinone dyes are given in Table I. Dyeing of nylon 66 and polyester fibres with all the dyes was carried out following a high temperature dyeing technique<sup>18</sup> using a glycerin bath "Laboratory High Temperature Dyeing Machine" containing twelve beakers. The absorption maxima of the disperse dyes (D<sub>1</sub>–D<sub>14</sub>) were recorded in DMF. The absorption maxima were in the range of 450 nm to 510 nm. The dyes were characterized by their infrared spectrum, all the dyes showed characteristic bands at 1559s cm<sup>-1</sup> (–N=N–) stretching. The dyes D<sub>5</sub> and D<sub>12</sub> showed a band at 836s cm<sup>-1</sup> for C–Cl stretching. The dye D<sub>8</sub>, D<sub>9</sub> and D<sub>10</sub> showed a broad band at 2240–2260 cm<sup>-1</sup> for (–C≡N) stretching.

These dyes were applied on nylon 66 and polyester fibres as disperse dyes, which gave variety of hues ranging from golden yellow, light brown to dark brown.

The data in Table I reveals that the position of the value of  $\lambda_{\max}$  depends on the nature of the substituents at the terminal amino group as well as on the phenyl ring. A bathochromic shift was observed, the magnitude of which depended on the nature of substituents at the terminal amino group. The following trend was observed.



Similarly, in case of cyano substituted derivatives of aniline, a bathochromic shift was observed in the following order:



A bathochromic shift was also observed on introduction of –NHCOCH<sub>3</sub> into the phenyl ring at the ortho position to the azo group (D-4 to D-7). A similar comparison of D-13 and D-14 also showed a bathochromic shift on displacing –NHCOCH<sub>3</sub> with –NHCOC<sub>2</sub>H<sub>5</sub>. Introduction of a methyl group in the phenyl ring ortho to the azo group also showed a bathochromic shift of 4 nm (D-4 and D-6). On the other hand, a hypsochromic shift was observed with the introduction of a chlorine group into the phenyl ring (D-4 to D-5 and D-11 to D-12).

TABLE II. Shade and fastness properties of novel 2-methyl-3-[3'-aminophthalimido]-4(3*H*)-quinazolinone disperse dyes

Dye	Light fastness		Washing fastness		Rubbing fastness				Perspiration fastness				Sublimation fastness	
	N*	P*	N*	P*	N*		P*		N*		P*		N*	P*
					Dry	Wet	Dry	Wet	Acidic	Alkaline	Acidic	Alkaline		
D <sub>1</sub>	3	3	5	5	5	5	5	5	5	5	5	5	5	5
D <sub>2</sub>	3	3	5	5	5	5	5	4	5	4	4	5	5	4
D <sub>3</sub>	3	3-4	4	5	5	4	5	5	4	5	5	5	5	5
D <sub>4</sub>	3	3	5	4	5	5	5	4	5	5	5	4	4	5
D <sub>5</sub>	3-4	3	5	5	5	5	5	5	5	5	5	5	5	5
D <sub>6</sub>	3	3	4	5	4-5	5	5	4-5	4	5	5	5	5	4
D <sub>7</sub>	4	3-4	4-5	5	5	4	4-5	4	5	4	5	4	5	5
D <sub>8</sub>	4	4	4	5	4	5	5	5	5	4-5	4	5	4	5
D <sub>9</sub>	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5
D <sub>10</sub>	4-5	4	5	5	5	5	4	5	5	5	5	5	5	4
D <sub>11</sub>	4	4-5	5	5	4	5	5	4	5	5	5	5	5	5
D <sub>12</sub>	4	4	5	4	5	4	5	5	4	5	4	5	5	5
D <sub>13</sub>	3	3	4-5	5	4	5	5	5	5	4	5	4	4	5
D <sub>14</sub>	3	3	4-5	4	5	5	5	4	5	5	5	5	5	5

N\* – nylon, P\* – polyester

The data of percentage exhaustion on the nylon 66 and polyester fibres were calculated by a known method<sup>19</sup> and are given in Table I. The higher percentage exhaustion on the nylon 66 fibres is to be expected due to its relatively open structure.<sup>20</sup>

Data of the fastness properties given in Table II show that the light fastness ranges from fair to fairly good to good for all the disperse dyes. The higher the rating is, the better is the fastness. The fastness to washing, rubbing, perspiration and sublimation are very good to excellent for all the prepared disperse dyes. The fastness to washing was determined using cotton fabric for the evaluation of the staining. This indicates the good penetration and affinity of these disperse dyes for the fibres.

#### CONCLUSION

Disperse dyes based on 2-methyl-3-[3'-aminophthalimido]-4(3*H*)-quinazolinone were synthesized. These dyes gave mostly golden yellow and light brown to dark brown shades on nylon 66 and polyester fibres having very good to excellent washing fastness properties on both substrates. The dyes have better exhaustion on nylon than on polyester, probably due to the greater accessibility of the pore structure in nylon.

*Acknowledgement:* One of the authors (Vijay H. Patel) is thankful to the Gujarat Government for a Research Fellowship.

#### ИЗВОД

#### ДИСПЕРЗНЕ БОЈЕ ЗАСНОВАНЕ НА ДЕРИВАТИМА 2-МЕТИЛ-3-[3'-АМИНОФТАЛИМИДО]-4(3*H*)-ХИНАЗОЛИНОНА

VIJAY H. PATEL, MANISH P. PATEL and RANJAN G. PATEL

*Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat, India*

Синтетизоване су нове хетероцикличне дисперзне боје сукцесивним диазотовањем 2-метил-3-[3'-аминофталимидо]-4(3*H*)-хиназолинона и купловањем са различитим моно- и ди-*N*-супституисаним дериватима анилина. Све дисперзне боје окарактерисане су својим процентним приносом, тачком топљења, UV-Vis спектром, елементалном анализом и IR спектром, као и способношћу бојења влакана од најлона 66 и полиестара. Процентно исцрпљивање купатила за бојење различитих влакана показало се релативно добро и прихватљиво. Обојена влакна показала су добру до врло добру отпорност на светлост, као и врло добру до одличну отпорност на прање, трљање, зној и сублимацију.

(Примљено 10. јануара, ревидирано 27. јула 2002)

#### REFERENCES

1. G. Back, A. Bhehler, (Ciba-Geigy A-G) German Offen; (1971) 2,236,269; [C.A. **79** (1973) 6752]
2. H. Sygiyama, T. Chinuki, T. Ikeda, H. Otsuka (Sumiomo Chemical Co. Ltd.) Japan (1964) 5673 [C.A. **76** (1967) 8249m]
3. E. Fleckenstein, R. Mohr, Ger. Offen, (1975) 2,347,756 [C.A. **83** (1975) 81207]
4. J. R. Geigy A-G, Brit, (1957) 784,665 [C.A. **52** (1958) 6203]
5. H. Pfitzner, W. Damert, (Badische Aniline and Soda Fabric A.G) Ger. Offen, (1972) 2,044,624 [C.A. **77** (1972) 36381]
6. S. Panosoua, J. Klichar, Sb. Ved Preci; Vysoka Skola Chem. Technol Pardubice, pt. 1 (1961) 70–82 [C.A. **58** (1963) 5813]

7. H. Weldinger, G. Lange, G. Wellenreuther; (Badische Aniline and Soda Fabrik A-G) Belg. (1963) 618,973 [*C.A.* **59** (1963) 11701]
8. A. Arcoria, *Ann. Chim. (Rome)*, **58** (1983) 1172 [*C.A.* **70** (1969) 107491]
9. G. Scarlata, (Atanio Intal) Boll Sedute Accad Gioeonia Sci., Natur Catania, **10** (1969) 53 [*C.A.* **73** (1970) 57124e]
10. A. A. Fada, H. A. Etman, F. A. Amer, M. Barghout, Kh. S. Mohamed; *J. Chem. Technol. Biotechnol.*, **61** (1994) 343 [*C.A.* **122** (1995) 83696q]
11. V. J. Patel, R. G. Patel, V. S. Patel; *Indian J. Text. Res.* **17** (1992) 45
12. L. A. Shemchuk, *Russ. J. Org. Chem.* **34** (1998) 534
13. J. Klosa, *J. Prakt. Chem.* **14** (1961) 84 [*C.A.* **56** (1962) 2449h]
14. *Org. Poluprod. i Krasiteli*, Nauch-Issledovetel. Inst. Org. Poluprovod. i Krasitelei im. K. E. Voroshilova, Sbornik Statei, No. 1, 196–206 (1959)
15. L. A. Errede, H. T. Oien, D. R. Yarian, *J. Org. Chem.* **42** (1977) 12
16. R. K. Vaid, B. Venkateswara Rao, B. Kaushik, S. P. Singh, *Indian J. Chem.* **26B** (1987) 376
17. H. Guenter, D. Johannes, F. R. Patel (1964) 361, 778, (Badische Aniline and Soda Fabrik A-G) [*C.A.* **61** (1964) 14682b]
18. K. B. Thakor, R. G. Patel, V. S. Patel, *Indian J. Fibre Text. Res.* **19** (1994) 84
19. K. Erik, in *The Analytical Chemistry of Synthetic Dyes*, K. Venkataraman Ed., Wiley, New York, 1977, p. 524
20. V. H. Patel, M. P. Patel, R. G. Patel, *Dyes and Pigments* **52** (2002) 191.



