

# Synthesis, Characterization, and Application of Hetarylazo Disperse Colorants: Preparation and Properties of Ink-Jet Inks with Active Agents for Polyester Printing

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**ABSTRACT:** The synthesis and characterization of two hetarylazo disperse colorants are described. These compounds were used for the preparation of ink-jet inks with and without active agents for polyester printing. The viscosity, conductivity, surface tension, and pH of these inks were studied over a period of time and discussed with respect to their structure and the active agent content. The particle size and particle size distribution of a representative ink containing a new synthesized hetarylazo compound were measured. All the prepared inks were proved to be suitable for ink-jet printing in terms of their particle size. Viscosity, surface tension, conductivity, and pH values of all inks, with and without active agent, were monitored over a period of 90 days and were related to the ink stability. The same properties were measured for an ink preparation with a commercial dye for comparison. The

inks containing the new synthesized dyes were found to be more advantageous regarding most of the above properties, i.e., surface tension, viscosity, and conductivity. Contrarily pH values of all the preparations were unacceptable for ink-jet inks. The ink compositions containing the new synthesized compounds were applied by exhaustion (dyed) on polyester fabric. Fastness properties of the dyed polyester samples were excellent to very good in most cases. Color measurements of the dyed fabric were also performed. A qualitative determination of the aromatic active agent adsorbed on the fiber by the exhaustion method was achieved by the GC-MS method. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** dyes/pigments; particle size distribution; polyesters; synthesis; active agent; cosmetotextiles

## INTRODUCTION

Ink-jet printing is presently one of the fastest growing imaging technologies; in addition to other advantages, it is more eco-friendly, requires low water and energy consumption, and has no or minimal residue dye waste in comparison with conventional printing technologies.<sup>1</sup>

Disperse dyes are used as coloring agents in the preparation of water-based ink-jet inks for polyester textile printing. Successful addition of active agents in the ink formulation would give special properties to it. Incorporating successfully an active ingredient as a component in an ink according to the ink-jet requirements is a challenge to the producer. It gives the possibility of producing innovative personalized finished articles, the so called "cosmetotextiles," reducing the production stages and minimizing waste water and energy consumption. This fact in combination with the water-based inks is in agreement with the requirements for environmentally

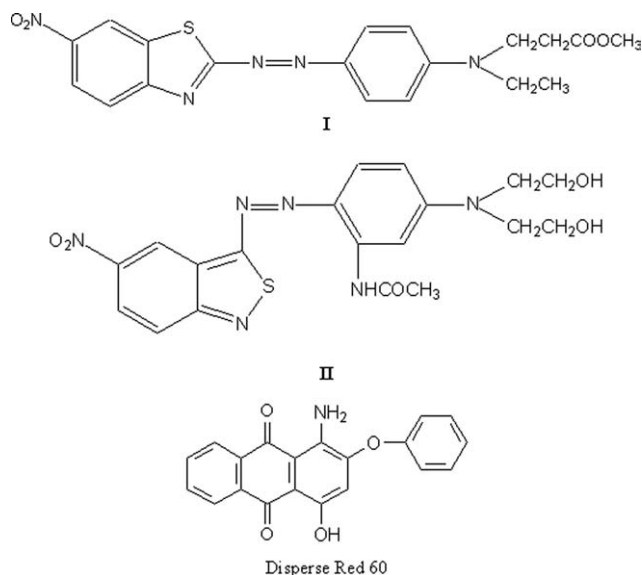
friendly processes and products. Cosmetotextiles represent a fast growing field related both to the textile and cosmetics industry. These are holding a specific amount of cosmetic substance meant to be released totally and instantly on the human body

Water-based ink-jet inks offer environmental advantages over their nonaqueous-based counterparts through reduced emission of volatile organic compounds that otherwise are present in solvent-based formulations. With environmental considerations continuing to have ever-greater impact upon industry and legislation textile, producers have to examine carefully the environmental impact of the products used. Water-based inks contain typically 30–80% water as a proportion of the total mass of the ink together with a water miscible organic solvent such as monohydric alcohol and the colorant (e.g., disperse dye), and a surface active agent which in the case of disperse dyes acts as a dispersant for the dye in the aqueous medium.<sup>2,3</sup>

Similar disperse colorants have been synthesized and used previously for the dyeing of cellulose acetate fibers. Preparation of analogous ink-jet inks was also done and discussed.<sup>4</sup>

Using heterocyclic dyes for ink-jet printing is a rather recent idea.<sup>1,5–7</sup> Particularly dyes derived from benzothiazole-, benzisothiazole ring are

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**Figure 1** Structure of the compounds **I**, **II** and the commercial dyes Disperse Red 60.

advantageous with respect to their potential use as commercially competitive replacements on environmental and economic considerations for established anthraquinone dyes.<sup>8,9</sup> In the search for colorants of high fastness and reduced environmental impact, the dyes of this work are expected to exhibit greatly improved fastness to light and dry heat on polyester fiber, while they permit the use of more environmentally friendly processing: only alkali is required as a discharging or clearing agent obviating the need for heavy metal salts and sodium hydrosulfite, respectively.<sup>10</sup> Because of the strong electron acceptor heterocyclic ring, the dyes show a significant bathochromic shift compared to their phenylazo counterparts, thus being useful for providing blue azo dyes.

In continuation to our previous work on the synthesis of hetarylazo disperse dyes and preparation of ink-jet inks for polyester printing, two similar dyes were synthesized and characterized.<sup>4,11–13</sup> These hetarylazo compounds **I**, **II** (Fig. 1) were used for the preparation of water-based ink-jet inks with (formulations 1',2') and without (formulations 1,2) the addition of active ingredient.

Ink-jet inks must be carefully formulated to ensure that they attain the correct balance of physical and chemical properties for high-speed application through the fine nozzles of the printing head. Typical physiochemical properties crucial to the suitability of these inks are the viscosity, surface tension, conductivity, pH, and particle size distribution. These properties were monitored over a period of 90 days.<sup>14–16</sup> The active ingredient used in this work was a fragrance, lemonene microcapsules. The same properties were measured for the reference ink

(without active ingredient) and an ink with a commercially available disperse dye. The results were compared and discussed. The inks were applied by exhaustion on polyester fabric.

Fastness properties of the dyed polyester samples were evaluated, and color measurements and qualitative determination of the aroma microcapsules adsorbed on the samples were made.

## EXPERIMENTAL

### Materials and methods

The following amines were commercially available and used without further purification: 2-amino-6-nitro-benzothiazole, 3-amino-5 nitro[2,1]benzothiazole (Zhejiang, China). Double-Jersey 100% polyester fabric white 190 g m<sup>-2</sup> supplied by Greuter-Jersey AG (Switzerland). Commercial grade 2-propanol (Fluka) and ethylene glycol (Riedel-de-Haen, Germany) were used. Alcoospers LFD (KYKE HELLAS SA) a condensation product of formaldehyde-sulfonic acid sodium salt was used as dispersing agent. Lemonene microcapsules (Speciality Textile Products, UK) were used as fragrance additive. The commercially available dye Disperse Red 60 (Yorkshire Colors, Germany) was used for comparison.

### Synthesis and characterization procedures

Melting points were obtained with a Koffler hot stage apparatus and are given uncorrected. UV-visible spectra were recorded with a Shimadzu UV spectrometer using methanol as solvent.<sup>1</sup>H-NMR data were obtained with a Bruker 300 AM spectrometer using CDCl<sub>3</sub>/d<sub>6</sub>-DMSO as solvent, and TMS as internal standard. Mass spectra were measured with a VG-TS 250 spectrometer. Elemental analyses were obtained using a Perkin Elmer 2400-II Element Analyzer.

### Synthesis and analytical data of azo compounds **I** and **II**

These compounds were prepared by the diazotization of amines 2-amino-6-nitro-benzothiazole and 3-amino-5 nitro[2,1]benzothiazole followed by coupling with 3-acetylamino-*N,N*-di-β-hydroxyethylamine and *N*-ethyl-*N*-acetoxethylamine.<sup>11,12</sup>

#### I

Yield of crude product 82%: purified by recrystallization (ethanol); m.p. 150–152°C; λ<sub>max</sub> (nm, CH<sub>3</sub>OH): 532.0; ε<sub>max</sub> (l mol<sup>-1</sup> cm<sup>-1</sup>, CH<sub>3</sub>OH):80645; <sup>1</sup>H-NMR (δ, CDCl<sub>3</sub>/d<sub>6</sub>-DMSO): 1.26 t (3H, H-b'), 2.72 t (2H, H-b), 3.58 q (2H, H-a'), 3.74 s (3H, H-c), 3.81 t (2H, H-a), 6.78 d (2H, H-3', H-5'), 8.01 d (2H, H-2', H-6'),

TABLE I  
Disperse Ink Formulation

Formulation	Dye (%)	H <sub>2</sub> O (%)	Alcohol (%)	Wetting agent EG (%)	Dispersing agent (%)	Fragrance microcapsules (%)
1	I/1	70	20	5	5	–
1'	I/1	70	20	5	5	0,5
2	II/1	70	20	5	5	–
2'	II/1	70	20	5	5	0,5

8.11 d (1H, H-4), 8.33 dd (1H, H-5), 8.75 d (1H, H-7); MS (*m/e*, %): 413(100 M<sup>+</sup>), 397(26), 366(25), 352(18), 352(18), 339(49), 312(90), 207(52), 195(87); C (%), calcd, found): 55.20, 55.35; H: 4.63, 4.49; N: 16.94, 16.89.

## II

Yield of crude product 90%: purified by recrystallization (ethanol); m.p. 160–163°C;  $\lambda_{\max}$  (nm, CH<sub>3</sub>OH): 613.0;  $\epsilon_{\max}$  (l mol<sup>-1</sup> cm<sup>-1</sup>, CH<sub>3</sub>OH): 52083; <sup>1</sup>H-NMR ( $\delta$ , CDCl<sub>3</sub>/*d*<sub>6</sub>-DMSO): 2.08 s (3H, H-4''), 3.75 t (4H, H-b), 4.36 t (4H, H-a'), 4.78 bs (2H, H-c), 6.48 d (3H, H-1'), 7.59 d (1H, H-7), 7.70 d (1H, H-6'), 8.00 s (1H, H-3'), 8.09 dd (1H, H-6), 8.85 d (1H, H-4) 9.40 bs (1H, H-4'); MS (*m/e*, %): 219(6), 195(6), 91(38), 70(100); C (%), calcd, found): 51.27, 51.34; H: 4.46, 4.54; N: 18.26, 18.91.

## Ink formulation

In Table I, the water-based ink formulations containing 2% w/v dye, 70% v/v H<sub>2</sub>O, a mixture of 2-propanol (IPA)/ethylene glycol (EG) 20/5 v/v as the miscible solvent, and 5% w/v dispersing agent are given. The mixture of ingredients was stirred for 30 min with an Ultra Turax T18 basic apparatus (IKA WERKE GmbH, Staufen, Germany) as a dispenser at 18,000 rpm and then using a Sonicator UP100H (Hilscher, USA) homogenizer. An amount 0.5% V/V of the active agent was added in the inks prepared using a Sonicator UP100H (Hilscher). In Table I, the reference formulations (without active agent) are also included.

## Surface tension conductivity, viscosity, and pH measurements

Surface tension measurements were made using a KSV Sigma 70 tensiometer (KSV Instruments, Helsinki, Finland) fitted with a De Nouy platinum ring. Conductivity measurements were performed using a Crison Conductimeter Basic 30 (Barcelona, Spain), and pH measurements were made using a WTW Microprocessor 535 pH meter (LA, CA); viscosity measurements were made using a Viscostar plus+ H (Fungilab, Barcelona, Spain) viscometer. The

above properties were measured at room temperature and atmospheric pressure for 1, 7, 14, 28, 60, and 90 days.

## Particle size distribution

The average particle size of the samples was measured at 25°C by dynamic light scattering using a Zetasizer (Malvern, UK) particle size analyzer. The dispersant viscosity and the refractive index were 0.887 cP and 1.33, respectively.

## Dyeing

Dyeing was carried out in a Rotadyer dyeing machine (John Jeffreys Ltd, Rochdale Banbury, UK) with a depth of dyeing 3% o.m.f. in a liquid ratio of 20 : 1 pH 4 at 130°C for 60 min. The dyed samples were then rinsed in cold water and reduction cleared using a solution comprising 2g L<sup>-1</sup> sodium dithionite and 1.5 g L<sup>-1</sup> sodium carbonate at 60°C using a liquor ratio of 20 : 1 for 20 min. The reduction cleared samples were rinsed in water and allowed to dry in the open air (Fig. 2).

## Fastness tests

Wash fastness of the dyeings was carried out according to BS1006:1990CO2 test, whereas light fastness was carried out according to BS1006:1990BO2 test.<sup>17</sup>

## Color measurements

The reflectance values of the prints and dyeings were measured using a Macbeth Color Eye 3000 spectrometer (Williamston, SC) under D65 illumination, 10

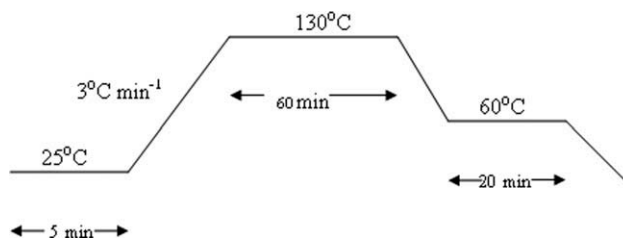
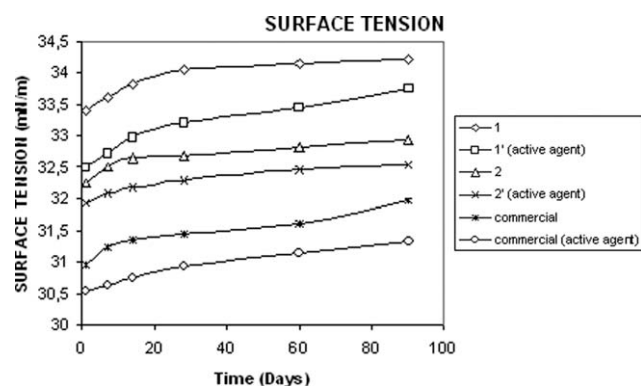


Figure 2 Dyeing and reduction clearing process of polyester fibers.



**Figure 3** Plots of surface tension values vs. time for the ink formulations 1',2' with active agent, 1,2 without active agent the inks containing the commercial dye with and without active agent.

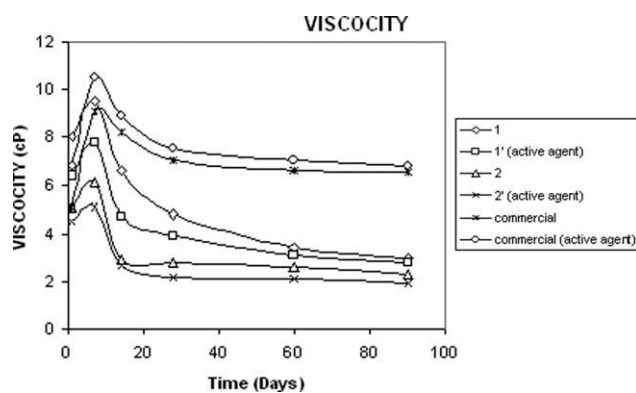
standard observer with UV included and specular component excluded. The CIE1976  $L^*a^*b^*C^*H^*$  coordinates and the  $K/S$  values were calculated from the reflectance values at the appropriate  $\lambda_{\max}$  ( $\lambda_{\max}$  Disperse Red 60 = 516.0 nm).

#### Qualitative determination of the fragrance adsorbed on the dyed polyester sample

Qualitative identification of the fragrance microcapsules was made by a GS-6890N gas chromatography. A total of 6 mL of distilled water was added to 0.3 g sample in a glass screw-top test tube. Then, 2 mL of hexane was added and mixed vigorously using a vortex mixer for 1 min at room temperature. The mixture was next heated at 90°C for 30 min with intermittent shaking; finally, the hexane layer was decanted. The aroma components extracted in the hexane layer were analyzed by a gas chromatograph (model GS-6890N, Agilent Technologies, Palo Alto, CA), using methyl butyrate as an internal standard. The samples were analyzed three times, and the data were presented as an average value. The operating conditions for the gas chromatography analysis were as follows: capillary column HP-FFAP from fused silica with polar immobile phase (0.20 mm i.d.  $\times$  25m length, 0.30- $\mu$ m-film thickness, Hewlett Packard USA).<sup>18</sup>

## RESULTS AND DISCUSSION

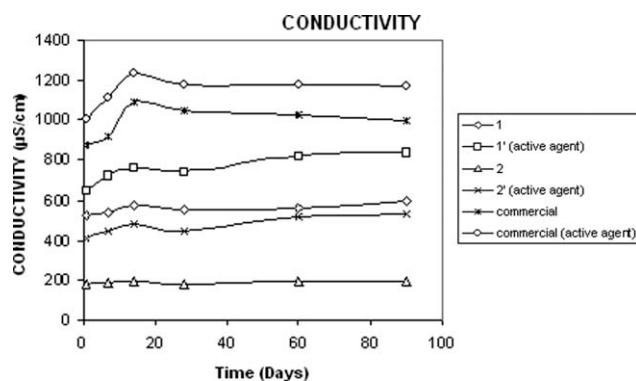
The compounds **I**, **II** were synthesized by coupling a diazotized heteroarylamine with *N*-substituted hydroxyethylaniline and acetoxyethylaniline (Fig. 1).<sup>11,12,19</sup> Heteroaromatic amines were selected as diazo components because the heterocyclic ring is a powerful electron-withdrawing residue. Derivatives of thiazole and isothiazole, i.e., heterocyclic systems containing sulphur as the  $\pi$ -excessive heteroatom, represent a very electronegative diazo component,



**Figure 4** Plots of viscosity values vs. time for the ink formulations 1',2' with active agent, 1,2 without active agent the inks containing the commercial dye with and without active agent.

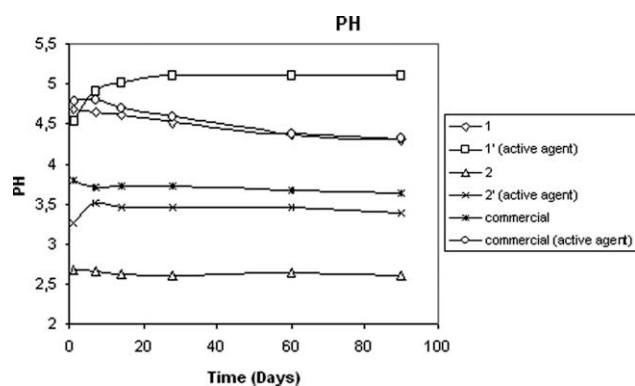
thus having a strong bathochromic effect, perhaps due to the d-orbitals of sulphur atom.<sup>20,21</sup> Thus, thiazole-isothiazole ring systems are particularly useful for providing blue dyes. Coupling with a benzene ring such as in **I** (Fig. 1) an intense red-blue is achieved. The isothiazole ring (**II**) is more bathochromic thus **II** is blue. The colorants **I,II** were used for the preparation of conventional ink formulations, and their viscosity, surface tension, and pH conductivity values were measured over a period of 90 days. Monitoring these properties of a formulation over a period of time is a widely accepted method for evaluating dispersion stability. The surface tension, viscosity, conductivity, and pH values of the inks prepared vs. time are given in Figures 3–6.

1. Inks for application via ink-jet printing should have a surface tension in the range of 21–48 or 30–60  $\text{mN m}^{-1}$ .<sup>21</sup> It can be seen from Figure 3 that all the inks prepared had a surface tension within the operational range with a slight increase until day 14, then remaining constant over the relevant period of time.



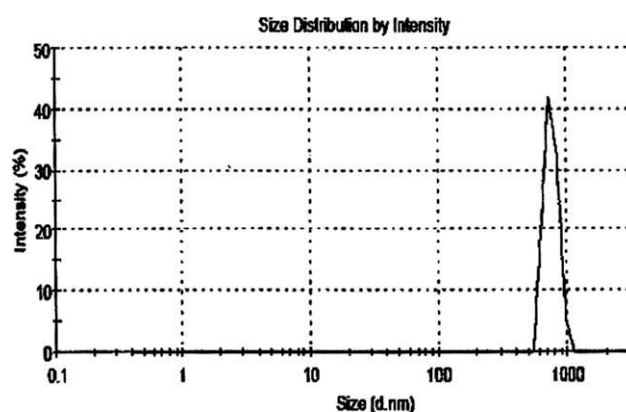
**Figure 5** Plots of conductivity values vs. time for the ink formulations 1',2' with active agent, 1,2 without active agent the inks containing the commercial dye with and without active agent.





**Figure 6** Plots of pH values vs. time for the ink formulations 1, 2' with active agent, 1, 2 without active agent the inks containing the commercial dye with and without active agent.

- It is generally accepted that ink-jet inks should have a viscosity lower than  $2cP^{22}$ , although it is not unknown for such inks to have a viscosity up to  $3cP$ .<sup>23</sup> Viscosity values of the inks 1 and 2 (inks without active agent) presented a maximum (day 8) and then reduced sharply with time (day 20) and remained stable vs. time (90 days, Fig. 4). The corresponding formulations with lemonene microcapsules presented lower viscosity values with the same curve shape.
- Conductivity values of the prepared inks are given in Figure 5. Dispersing agent and colorant structure affect the conductivity values as expected. Alcoospers LFD, an ionic dispersing agent used for the conventional inks plays a dominant role in the relatively high values of conductivity measured for these inks. Ink prepared with the **II** having *N,N*-bis-hydroxyethylaniline as a coupling component had the highest conductivity, may be due to the potential ionization of the two in the aqueous solution. Thus, acetylation of one hydroxy group (**I**) results in a significant reduction in conductivity.
- The composition of the dispersion determines the pH (Fig. 6). Apparently, because of the acetylation of the ionizable hydroxy groups,



**Figure 7** Particle size distribution of ink 1 containing compound I.

ink 1 has the highest pH value, although remaining lower than the acceptable neutral region for ink-jet printing.<sup>15</sup> In this case, pH correction with a buffer solution is necessary to use them as ink-jet inks. Addition of lemonene microcapsules results in an increasing in pH values in both cases (ink 1' and ink 2') remaining though still not acceptable (Fig. 6).

Consequently, a similar increase is observed also in the corresponding conductivity values (Fig. 5)

The same measurements were made with the commercial dye Seriplas Red 2BL (CI Disperse Red 60,  $\lambda_{max}$  516 nm) (Figs. 3–6). The following are concluded from the Figures 3–6:

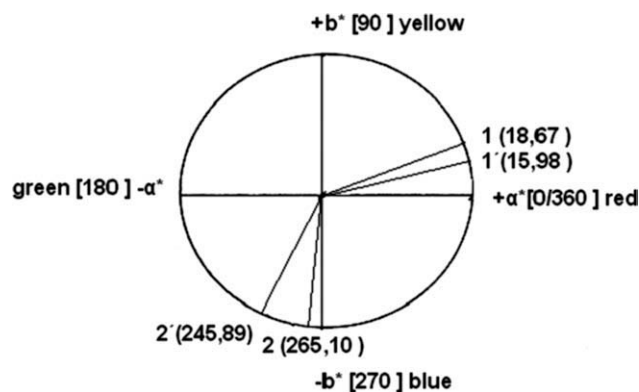
Surface values are in the acceptable range for ink-jet inks<sup>24,25</sup> in all cases (commercial and new synthesized dyes) remaining satisfactorily stable. Surface tension values of the inks containing the new synthesized inks were higher than those of the inks with the commercial dye. This is in favor of their adhesion wettability (Fig. 3)

Viscosity curves shape is similar for the inks with both commercial and new synthesized dyes: a maximum (day 8) and then sharp reduce with time (day 20) and stable vs. time (90 days, Fig. 4). However, viscosity values of commercial dye preparations are unacceptably high for ink-jet inks,<sup>24,25</sup> while the

**TABLE II**  
K/S Values and Color Coordinates for the Wool and Polyamide Fibers Dyed with the Compounds 1, 1', 2, 2'

Sample	K/S	$\lambda_{max}$ (nm)	$L^*$	$a^*$	$b^*$	$C^*$	$H^*$
1	25.32	510	18.68	10.80	2.69	17.09	18.67
1'	25.46	510	17.66	9.58	1.92	15.56	15.98
2	20.38	620	17.79	-0.42	-6.66	120.30	265.10
2'	20.29	620	18.06	-1.7	-3.03	5.78	245.89

1, Sample dyed with ink containing compound 1; 1', Sample dyed-printed with ink containing compound 1 + 0,5% fragrance; 2, Sample dyed with ink containing compound 2; 2', Sample dyed-printed with ink containing compound 2 + 0,5% fragrance.



**Figure 8** Color circle and hue angles of formulations 1, 1' and 2, 2' on polyester fiber.

corresponding final values (up to day 20) are in the acceptable operational range for ink-jet inks (2–3cP, Fig. 4).

Conductivity values of the commercial dye ink preparations are significantly higher ( $870\text{--}1230\ \mu\text{S cm}^{-1}$ ) than the corresponding hetarylazo dyes preparations ( $180\text{--}840\ \mu\text{S cm}^{-1}$ ). Given that conductivity values of the ink preparations should be remained as low as possible, the new hetarylazo ink preparations are advantageous compared to the commercial ones (Fig. 5).

Contrarily pH values of the inks with the compounds **I,II**, references or/and with the active agent lemonene microcapsules present a better stability with time, although pH values in this case are lower (2.5–5) than the corresponding of the commercial dye (4.3–4.7). In both cases, pH values are unacceptable for ink-jet inks, and a pH correction is necessary (Fig. 6). Conclusively, the inks containing the new synthesized dyes were found to be more advantageous regarding most of the above properties, i.e., surface tension, viscosity, and conductivity.

To evaluate the particle size distribution of the ink containing the compound **I**, dynamic light scattering

measurements for this composition was performed. Figure 7 represents the size distribution by intensity of the ink containing the compound **1** (at preparation day 1). It appears as a peak at 917.3 nm (100%). This property is as crucial for the suitability of an ink-jet ink as the above set of rheological properties measured because they enable optimum droplet formation within and through the fine nozzles of the printing head.

All the inks prepared were checked successfully by passing through a 1- $\mu\text{m}$  filter indicating their ink-jet suitability.

It was also decided to apply the ink-jet printing inks on polyester also by exhaustion to investigate if the presence of solvents could have any beneficial effect during exhaustion dyeing. Obviously, the preparation of digital printing inks exclusively targets the market of digital printing. However, the good storage stability of ink-jet printing inks could also be beneficial for the production of stable liquid formulations of disperse dyes for conventional polyester dyeing and printing.

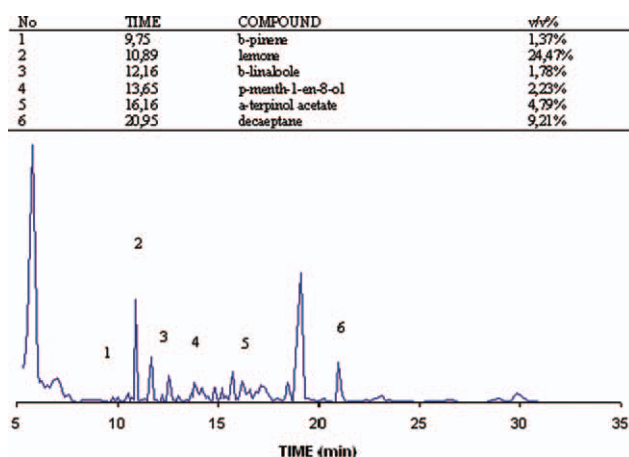
Thus, the ink compositions 1, 2, 1', 2' containing the compounds **I** and **II** were used to dye polyester fabric using the method shown in Figure 2, followed by reduction clearing. Table II shows the relevant colorimetric data and color strength values for the dyeings after reduction clearing. From Table II, the following are concluded:

The presence of lemonene microcapsules (formulations 1, 2') does not result practically in a differentiation in *K/S* values of the samples which remain satisfactorily high. The samples dyed with the formulations 1, 1' (inks containing the benzothiazole compound **I**) with *h* values 18.67 and 15.95° are in the red-yellow area (0–90°) in the color circle (Fig. 8), whereas the samples dyed with the formulations 2, 2' containing the benzoisothiazole compound **II** are in the green-blue color circle area (180–270°). This was also visually confirmed. The presence of aroma

**TABLE III**  
Fastness Properties of the Dyed Polyester Samples

Sample	Fastness							
	Light	Color change (CC)	Wash					Wool
			Color staining (CS)					
			Acetate	Cotton	PA	PES	PAN	
1	>7	5	2	2–3	3	4–5	5	5
2	>7	5	3	3–4	2	4–5	4	3
1'	>7	5	2–3	2–3	3–4	4–5	5	5
2'	>7	5	2	2–3	2	5	4	3

1, Sample dyed with ink containing compound **1**; 1', Sample dyed-printed with ink containing compound **1** + 0.5% fragrance; 2, Sample dyed with ink containing compound **2**; 2', Sample dyed-printed with ink containing compound **2** + 0.5% fragrance.



**Figure 9** GC-MS chromatogram of lemonene microcapsules. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

microcapsules in the formulation 2' (benzothiazole dye 2+lemonene microcapsules) resulted in a 60 nm shift of the  $\lambda_{\max}$  of the reflectance measurement (560 to 620 nm) in agreement with the significant increase in the corresponding  $h$  value ( $19.21^\circ$ ) toward the green area of the color circle.

The fastness data obtained for the dyed samples are given in Table III. The staining of the wool, polyester, and acrylic fibers in the multifiber strip were found to be 5 in most cases. Color change was also 5 in all cases. As it was expected, the man-made less hydrophilic fibers such as nylon and acetate were stained more by both disperse dyes. The natural fiber cotton with a medium hydrophilicity was also stained, whereas staining of wool with the highest hydrophilicity was very good (ink 2,2') to excellent (ink 1,1') as it was expected.

Finally, determination of the aroma microcapsules adsorbed on the dyed samples was made by extracting the microcapsules with hexane and analyzing the extract by gas chromatography.<sup>18</sup> The main relative peaks selected from the lemonene chromatogram with their appearance time and their peak area contribution in lemonene hexane extract are presented in Figure 9. From Figure 9, it is concluded that lemonene is the major constituent among other minor terpenoids in the hexane extract used for the chromatography as it was expected. The two major peaks observed in the chromatogram, the first at time < 1min and the second at time  $\approx$  20 min are attributed to the hexane solvent used and triethyl phthalate (a possible hexane extract ingredient from polyethylene terephthalate).

## CONCLUSIONS

Two hetarylazo disperse colorants were synthesized by diazotization of aminobenzothiazoles and benzoi-

sothiazoles and coupling with substituted hydroxyl ethylamine and acetoxyethylamine. Because of the strong electron acceptor heterocyclic ring in the diazo component, the dyes showed a significant bathochromic shift in comparison with their phenylazo counterparts.

The synthesized heteralazo dyes show distinct advantages versus the commonly used anthraquinone-based dispersed dyes in terms of light fastness ( $>7$ ), which makes them suitable for specialized application such as for automotive fabric interiors where the requirements for high light fastness dyes is very high.

The synthesized dyes were used for the preparation of ink-jet inks by adding lemonene microcapsules as an active agent. The viscosity, surface tension, conductivity, pH, and particle size distribution of these inks were studied over a period of time and discussed. All the prepared inks were proved to be suitable for ink-jet printing in terms of their particle size. Viscosity, surface tension, conductivity, and pH values of all inks, with and without active agent, were monitored over a period of 90 days and were related to the ink stability. The same properties were measured for an ink preparation with a commercial dye for comparison.

The inclusion of active ingredients in the ink formulations allows the production of specialized items with distinct properties and with the incorporation of the digital printing technology; this can be done economically when and where is needed allowing the production of articles with tailor unique properties.

To evaluate the particle size distribution of an ink containing one new synthesized hetarylazo dye, dynamic light scattering measurements for this formulation were performed, and the result confirmed the suitability of the inks for ink-jet printing (peak < 1  $\mu\text{m}$ ). The inks were applied by exhaustion to polyester fabrics. Fastness properties of the dyed polyester samples were evaluated, and color measurements were made. Qualitative and quantitative determination of the aroma (lemonene) microcapsules adsorbed on the polyester fiber were also made by GC-MS.

Ch. Koukiotis (LOUFAKIS CHEMICALS, Thessaloniki, Greece) conducted the particle size and particle size distribution measurements. Dr. G. Kalantzakis, Department of Food Chemistry, School of Chemistry, AUTH) conducted the GC-MS measurements for the lemonone identification

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