

Synthesis and Characterization of Hetarylazo Disperse Colorants: Preparation and Properties of Conventional and Microemulsified Inks for Polyester Ink-Jet Printing

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ABSTRACT: The synthesis and characterization of three hetarylazo disperse colorants are described. These compounds were used for the preparation of conventional inks and/or oil-in-water microemulsions (microemulsified dyes). The viscosity, conductivity, surface tension, and pH of these inks were studied over a period of time and discussed with respect to their structure. The particle size and particle size distribution of a representative

microemulsion were compared to those of a corresponding conventional ink. The measured properties were compared to the properties of commercially available inks. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1422–1427, 2010

Key words: dyes/pigments; particle size distribution; polyesters; synthesis

INTRODUCTION

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

The objective of this work was the synthesis of hetarylazo disperse compounds and their use as coloring agents in the preparation of ink-jet inks for polyester printing. Similar disperse colorants have been synthesized and used previously for the dyeing of cellulose acetate fibers.^{2–4}

Using heterocyclic dyes for ink-jet printing is a rather recent idea.^{1,5–7} In particular, dyes derived from benzothiazole and benzisothiazole rings are advantageous with respect to their potential use as commercially competitive replacements of established anthraquinone dyes for environmental and economic considerations.^{8,9} 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 fibers, and they will permit the use of more environmentally friendly processing: only an alkali is required as a discharging or clearing agent, eliminating the need for heavy metal salts and sodium hydrosulfite, respectively.^{10,11} Because of the strong electron-acceptor heterocyclic ring, the dyes show a significant bathochromic shift in comparison with their phenylazo counterparts, thus being useful for providing blue azo dyes.

These dyes were used for the preparation of conventional ink-jet inks. Ink-jet inks must be very 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.^{12,13}

To achieve improvements in these properties (mainly the particle size), oil-in-water microemulsions containing these hydrophobic colorants were also prepared with the microemulsification technique and a Gemini-type surfactant.¹⁴ Microemulsified dyes have attracted interest in the field of textiles, and disperse dyes are ideal for microemulsification.¹⁵

The viscosity, surface tension, conductivity, pH, and particle size distribution of these inks, both conventional and microemulsified, were studied over a period of time and discussed.

The same properties were also measured for a commercial disperse ink and an ink prepared with a commercially available disperse dye. The results were compared and discussed.

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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, and 3-acetylamino-*N,N*-di- β -hydroxyethylaniline (Zhejiang, China). A condensation product, formaldehyde/sodium salt of sulfonic acid (Alcoospers LFD, Kyke Hellas S.A., Thessaloniki, Greece), and a Gemini-type surfactant, *N*-decanoyl-*N*-methylglucamine (MEGA-10, Fluka, Buchs, Switzerland), were used as dispersing agents. Propanol-2 (Fluka) and ethylene glycol (Riedel-de-Haën, Buchs, Switzerland) were used for the ink formulation. The commercially available dye Seriplas Br Blue 3GN (Kyke Hellas) and Digistar PES HD magenta, cyan, black, and yellow inks (Polyprint S.A., Thessaloniki, Greece) were used as references.

Synthesis procedures

3-Acetylamino-*N,N*-di- β -acetoxyethylaniline was prepared by acetylation of 3-acetylamino-*N,N*-di- β -hydroxyethylaniline with acetic acid/acetic anhydride. Melting points were obtained with a Koffler (Reichert, Austria) hot stage apparatus and are presented uncorrected. Ultraviolet-visible spectra were recorded with a Shimadzu UV2101 (Shimadzu Scientific Instruments Inc., Maryland, Columbia) spectrometer with methanol (MeOH) as the solvent. $^1\text{H-NMR}$ data were obtained with a Bruker 300 AM (Bruker Daltonic GmbH, Bremen, Germany) spectrometer using CDCl_3 /hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) as the solvent and tetramethylsilane as the internal standard. Mass spectra were measured with a VG-TS 250 (Spectro Analytical Instruments Inc., NJ) spectrometer. Elemental analysis was obtained with a PerkinElmer 2400-II (Perkin-Elmer, USA), element analyzer.

Synthesis and analytical data of azo compounds 1–3

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 -hydroxyethylaniline, 3-acetylamino-*N,N*-di- β -acetoxyethylaniline, and *N*-2-hydroxyethyl-1-naphthylamine.² 3-Acetylamino-*N,N*-di- β -acetoxyethylaniline was prepared by the acetylation of 3-acetylamino-*N,N*-di- β -hydroxyethylaniline.

1

Yield of crude compound: 98%. mp: 228–230°C [ethanol (EtOH)]. λ_{max} (nm, MeOH): 554.5, deep red. $^1\text{H-NMR}$ (δ , $\text{CDCl}_3/\text{DMSO-}d_6$): 2.34s (3H, H-4''), 3.81t (4H, H-b), 3.87t (4H, H-a), 4.95bs (2H, H-c),

6.78d (1H, H-1'), 8.00d (1H, H-6'), 8.02d (1H, H-4) 8.22s (1H, H-3''), 8.29dd (1H, H-5), 8.74d (1H, H-7), 9.18bs (1H, H-4'). Mass spectrometry (MS; m/z , %): 296 (38), 263 (29), 91 (56), 43 (100). ANAL Calcd: C, 50.87%; H, 4.24%; N, 18.72%. Found: C, 50.34%; H, 4.54%; N, 18.91%.

2

Yield of crude product: 81%. mp: 195–197°C (EtOH). λ_{max} (nm, MeOH): 594.5, blue. $^1\text{H-NMR}$ (δ , $\text{CDCl}_3/\text{DMSO-}d_6$): 2.35s (3H, NHCOCH_3), 2.76t (4H, H-b, H-b'), 3.73s (6H, H-c, H-c'), 3.90t (4H, H-a, H-a'), 6.58t (1H, H-3'), 7.54s (1H, H-5'), 7.76d (1H, H-7), 8.19d (1H, H-2'), 8.21d (1H, H-6), 9.08s (1H, H-4), 9.36bs (1H, NHCOCH_3). MS (m/z , %): 528 (16, M^+), 527 (61, $[\text{M}-1]^+$), 455 (50), 442 (14), 337 (20), 264 (44), 207 (16), 195 (29), 55 (100). ANAL Calcd: C, 52.27%; H, 4.58%; N, 15.80%. Found: C, 52.28%; H, 4.78%; N, 15.52%.

3

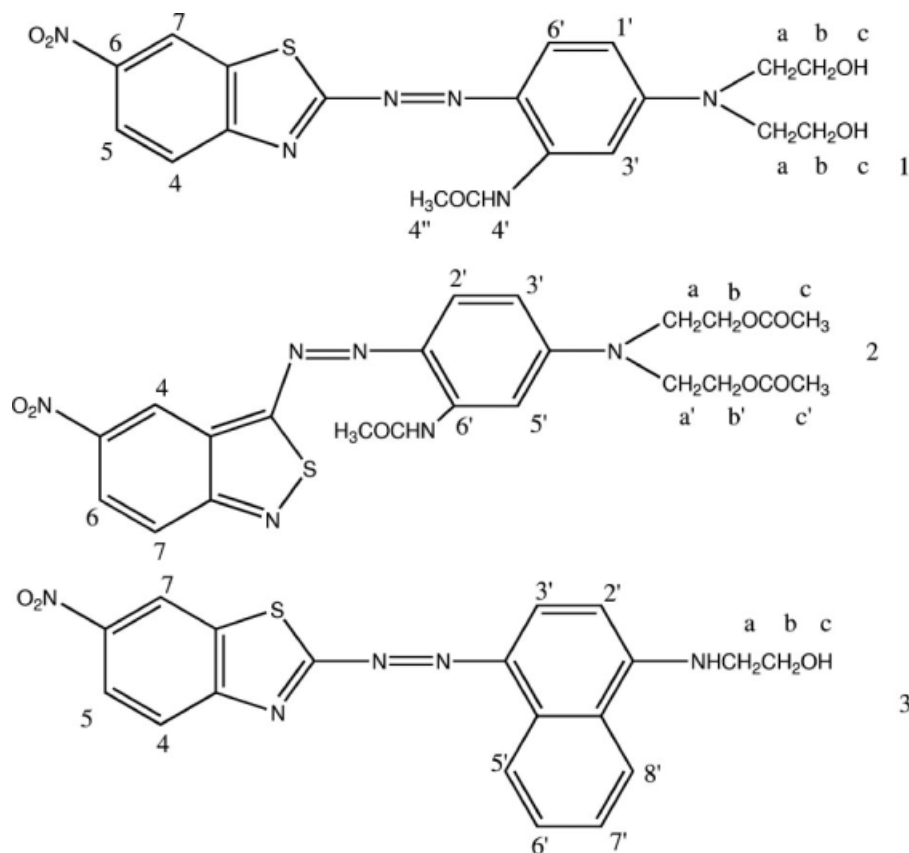
Yield of crude product: 99%. mp: 212–214°C (EtOH). λ_{max} (nm, MeOH): 597, blue. $^1\text{H-NMR}$ (δ , $\text{CDCl}_3/\text{DMSO-}d_6$): 3.27 broad s (1H, OH), 3.90t (2H, H-2'), 4.50t (2H, H-c), 6.91d (1H, H-2'), 7.56–7.72m (3H, H-6'–8'), 7.97d (1H, H-3'), 8.27d (1H, H-5), 8.39d (1H, H-4), 8.53dd (1H, H-5), 8.73d (1H, H-7). MS (m/z , %): 197 (31.7), 195 (87.8), 79 (14.0), 60 (21.1), 45 (43.9), 28 (100). ANAL Calcd: C, 58.00%; H, 3.84%; N, 17.86%. Found: C, 57.26%; H, 3.64%; N, 17.12%.

Ink formulation

Table I shows the general formulation employed for the preparation of the disperse inks. The mixture of ingredients with previous purification was stirred for 30 min with an Ultra Turrax T18 basic apparatus (IKA Werke GmbH, Staufen, Germany) as a disperser at 18,000 rpm. The inks were filtered with 1- μm filters (Domnick Hunter Industrial Division, England) at a pressure of 7.7 bar/g to ensure ink-jet suitability. Microemulsified inks were produced as follows: The hydrophobic colorant was dissolved in 10 mL of petroleum ether by stirring. *N*-Decanoyl-*N*-methylglucamine was dissolved in the ethylene glycol/propanol/water mixture by stirring. The organic phase (colorant solution) was added to the aqueous phase

TABLE I
Disperse Ink Formulation

	Quantity	%
Colorant	0.2 g	1
Propanol-2	30 mL	15
Ethylene glycol	10 mL	5
Alcoospers LFD	0.06 g	<1
Water	160 mL	80



Scheme 1 Structures of compounds 1–3.

(a MEGA-10 solution) to form a stable oil-in-water microemulsion with a Sonicator UP50H ultrasonic processor (Hilscher Ultrasonics GmbH, Teltow, Germany) at the maximum capacity of 20 Hz for 10 min.

Surface tension, conductivity, viscosity, and pH measurements

The surface tension measurements at equilibrium were determined with a Sigma 70 (KSV, Helsinki, Finland) tensiometer fitted with a De Nouy platinum ring. Conductivity measurements were recorded with a Crison Basic 30 (Crison Instruments SA, Barcelona, Spain) conductimeter, the pH was measured with a WTW pH 535 MultiCal (Wissenschaftlich-Technische Werkstaetten GmbH, Weinheim, Germany) microprocessor pH meter, and the viscosity was measured with a ViscoStar (Barcelona, Spain) +H Fungilab. These properties were measured over 1, 8, 30, and 90 days for both the conventional ones and the microemulsions at room temperature \pm 220°C and atmospheric pressure.

Particle size distribution

The average particle size of the samples was measured at 250°C by dynamic light scattering with a Zetasizer (Malvern Instruments Ltd., Worcester-shire, Malvern, United Kingdom; dispersant viscos-

ity = 0.887 cP, dispersant refractive index = 1.33–1.811, material absorption = 0.1). The particle size was taken as a mean of two measurements.

RESULTS AND DISCUSSION

Compounds 1–3 were synthesized by the coupling of a diazotized heteroarylamine with *N,N*-substituted ethylaniline and *N*-substituted 1-naphthylamine (Scheme 1).^{2–4,16} Heteroaromatic amines were selected as diazo components because the heterocyclic ring is a powerful electron-withdrawing residue. Derivatives of thiazole and isothiazole, that is, heterocyclic systems containing sulfur as the π -excessive heteroatom, represent very electronegative diazo components, thus having a strong bathochromic effect perhaps due to the *d*-orbitals of the sulfur atom.^{10,17} Thus, thiazole–isothiazole ring systems are particularly useful for providing blue dyes. Coupling with a benzene ring such as that in 1 (Scheme 1) weakens this effect, but an intense red is still achieved. The isothiazole ring (2) is more bathochromic, so 2 is blue, although the coupling component is a substituted benzene ring, whereas naphthalene-based intermediates as coupling components (3) compensate for this effect, and 3 is also blue.¹⁸ Colorants 1–3 were used for the preparation of conventional ink formulations, and their viscosity, surface

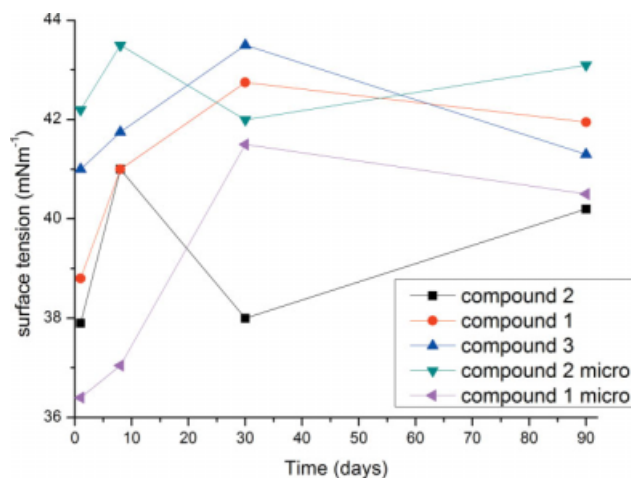


Figure 1 Surface tension versus time for the prepared inks. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tension, pH, and conductivity values were measured over a period of 90 days. The viscosity, surface tension, and conductivity values are given in Figures 1–3. The pH values for the same inks over the same period of time are given in Table II.

Inks for application via ink-jet printing should have a surface tension in the range of 21–48 or 30–60 mN/m.¹⁹ Figure 1 shows that all the prepared inks had a surface tension within the operational range that remained relatively constant over the relevant period of time.

It is generally accepted that ink-jet inks should have a viscosity lower than 2 cP,²⁰ although it is not unknown for such inks to have a viscosity up to 3 cP.²¹ Thus, all the prepared conventional inks were suitable for ink-jet printing in terms of viscos-

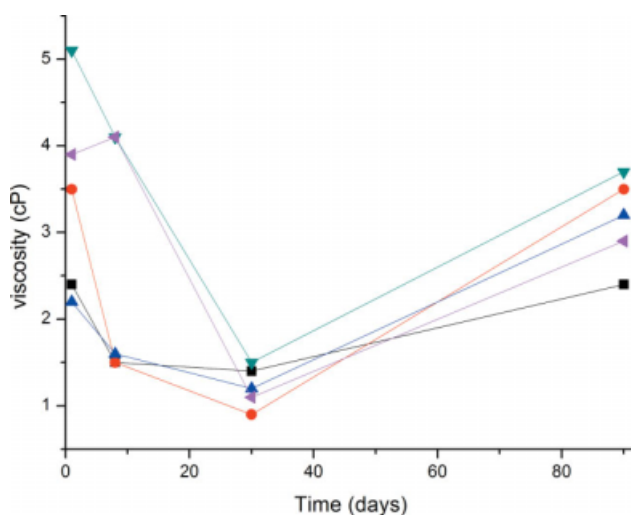


Figure 2 Viscosity versus time for the prepared inks (for the key, see Fig. 1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

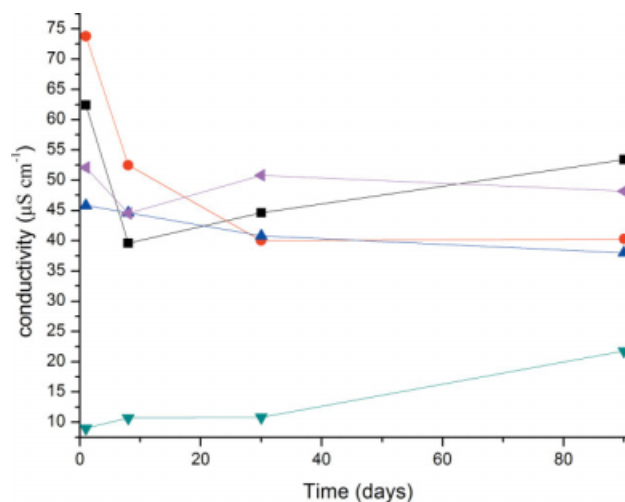


Figure 3 Conductivity versus time for the prepared inks (for the key, see Fig. 1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ity (Fig. 2). The viscosity values decreased with time, so after 8 days, the viscosity was in all cases lower than 2 cP.

The conductivity values of the prepared inks are given in Figure 3.

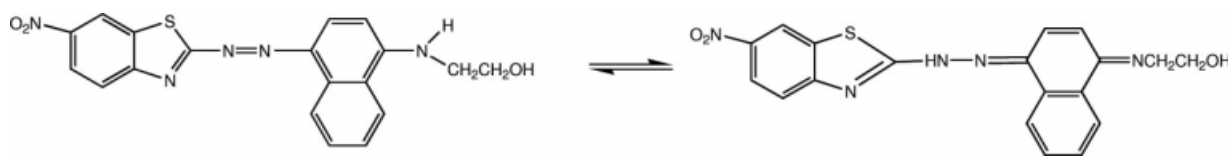
The dispersing agent and colorant structure affect the conductivity values as expected. Alcoospers LFD, an ionic dispersing agent used for the conventional inks, plays a dominant role in the relatively high conductivity values measured for these inks.

Ink prepared with 1 (having *N,N*-bishydroxyethyl-aniline as a coupling component) had the highest conductivity, perhaps because of the potential ionization of the two hydroxyl groups in the aqueous solution. Thus, acetylation of the two hydroxyl groups (2) resulted in a significant reduction of the conductivity.

The composition of the dispersion determines the pH. Because the naphthalene-based coupler (3) was more acidic than 1, ink 3 had the lowest pH of the

TABLE II
pH Values of the Prepared Inks

Compound	Time (days)	pH	
		Conventional	Microemulsion
1	1	4.26	2.83
	8	4.20	2.85
	30	3.51	2.89
	90	3.50	2.48
2	1	4.37	3.68
	8	5.26	6.83
	30	4.34	4.72
	90	3.88	3.85
3	1	3.15	—
	8	3.09	—
	30	2.82	—
	90	2.71	—



Scheme 2 Azo-hydrazo equilibrium.

three conventional inks over the time period measured. Apparently, again because of the acetylation of the ionizable hydroxyl groups, ink 2 had the highest pH value, which was close to the acceptable neutral region for ink-jet printing (Table II). In the opposite case (acidic inks), pH correction with a buffer solution was necessary for their use as ink-jet inks.

Particularly for 3, the pH had an influence on the azo-hydrazo equilibrium.¹⁸ An acidic pH favors the hydrazo form, and a basic pH favors the more stable azo form (Scheme 2). Compounds 1 and 2 practically exist only in the azo form and therefore are expected to be more light-fast.

Colorants 1 and 2 were used to produce thermodynamically stable oil-in-water microemulsions in which volatile oil droplets contained the dissolved water-insoluble colorant.^{14,22} The amount of the immiscible organic solvent was minimized and regenerated after the procedure. Thus, the inks were water-based and fulfilled specific environmental restrictions. The surface tension, viscosity, conductivity, and pH values of these inks measured over a period of 90 days are given in Figures 1–3 and in Table II.

Surface tension values for micro-inks 1 and 2 were in the acceptable range (Fig. 1).

Nonionic *N*-decanoyl-*N*-methylglucamine (MEGA-10), the dispersing agent used for the corresponding microemulsions, did not have the same effect as Alcoospers LFD in keeping the conductivity values of the emulsion significantly lower. Again, the conductivity of microemulsion 1 was higher than the

corresponding conductivity of microemulsion 2 (Fig. 3). Acceptable conductivity values for ink-jet inks are 6–12 mS/cm,¹⁹ so even microemulsion 1 had a relatively high conductivity value.

N-decanoyl-*N*-methylglucamine also affected the viscosity of the microemulsions, keeping the values relatively high (Fig. 2).

Micro-ink 2 had the highest pH values, like the conventional one, close to the acceptable neutral region, apparently because of the acetylation of the ionizable hydroxyl groups (Table II).

To evaluate the particle size distribution of conventional ink 2 and microemulsion 2, dynamic light scattering measurements for these two compositions were performed. Figure 4 presents the size distribution by the intensity of the oil phase of microemulsion 2, which contained colorant 2 dissolved in this phase. The bimodal distribution shown in Figure 4 (peak 1 with a mean diameter of 460.9 nm and an intensity of 90.64% and peak 2 with a diameter of 62.06 nm and an intensity of 9.358%) might be explained by the Ostwald ripening phenomenon observed in oil-in-water emulsions, which resulted in the diffusion of the dissolved molecules from smaller droplets to larger droplets because of the greater solubility of the molecule in the larger droplets during the 3-month shelf life of the material (the time of the particle size measurement). Thus, an original mean diameter of 62.06 nm (nanoscale material) became a dominant mean diameter of 460.9 nm (90.6%; microscale material), and this would be

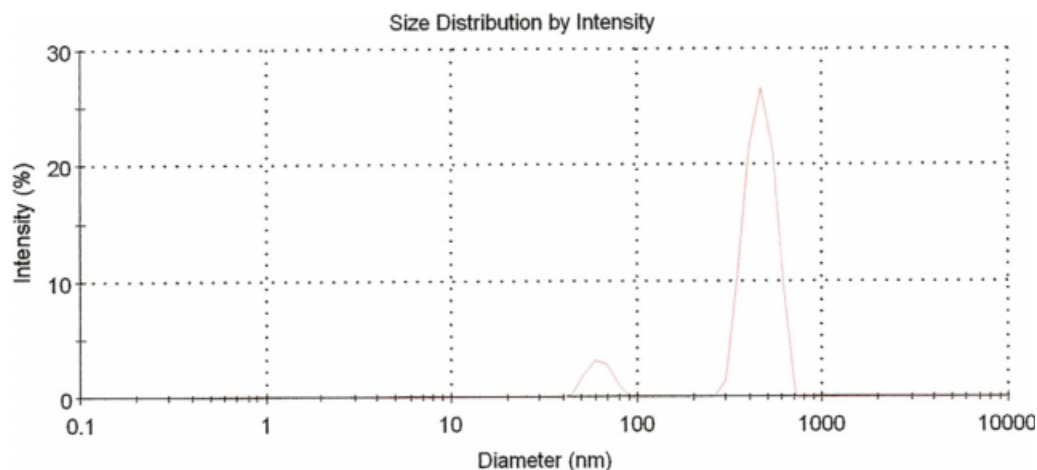


Figure 4 Particle size distribution of compound 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

acceptable for an ink-jet ink;¹² however, the particle size measurement of conventional ink **2** showed a bimodal size distribution, which also had a peak mean diameter of 361.9 nm and an intensity of 52.27% and a peak mean diameter of 1409 nm and an intensity of 47.72%.

Surface tension measurements performed for commercially available ink-jet inks (Digistar PES HD magenta, cyan, black, and yellow inks) demonstrated similar values for their surface tension (38.1–39.7 mN/m).

The conductivity values of a conventional ink prepared with the commercial dye Seriplas Br Blue 3GN (Kyke Hellas) and mixtures of propanol-2 and water (1/5 and 1/20) as solvents, measured under the same conditions, were found to be 358 and 57.9 mS/cm and were significantly higher than those of inks **1–3**, conventional and microemulsified especially, whereas the conductivity values for inks suitable for ink-jet printing should be minimized.^{19(b)}

The pH values of the commercially available Digistar PES HD inks were in the alkaline range (8.7–10.0), whereas the pH values of the Seriplas Blue inks were in the neutral region (7.4–7.6); this indicated that those inks do not need any pH correction or pH control with a buffer solution.^{19(a)}

The particle size distributions of the inks prepared with Seriplus Blue, both conventional and microemulsified, were as follows:

Conventional: Peak 1, 4301 nm (65.43%); peak 2, 756.2 (34.57%).

Microemulsion: Peak 1, 891.3 (93.44%); peak 2, 171.0 (6.56%).

Thus, a significant improvement, mainly in the conductivity and particle size distribution, was concluded from the comparison of inks **1–3** and the commercial ink Seriplus Blue, both conventional and microemulsified.

CONCLUSIONS

Three hetarylazo disperse colorants were synthesized by diazotization of aminobenzothiazoles and benzoisothiazoles and coupling with substituted hydroxyl ethylamine, acetoxylethylamine, and 1-naphthylamine. 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. These dyes were used for the preparation of conventional ink-jet inks. 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 conventional inks were suitable for ink-jet printing in terms of the viscosity

and surface tension. The conductivity and pH values were discussed with respect to the colorant structure, which affected these values as expected. Two of the colorants were used to produce thermodynamically stable oil-in-water microemulsions in which volatile oil droplets contained the dissolved water-insoluble colorant, and the properties of the microemulsions were also studied and found to be improved in comparison with the conventional ones. To evaluate the particle size distribution of one conventional ink and the corresponding microemulsion, dynamic light scattering measurements for these two compositions were performed, and a significant improvement in the particle size distribution was concluded from the comparison of the conventional and microemulsion inks. The viscosity, conductivity, surface tension, and pH were studied over a period of time for commercially available inks and inks prepared with a commercial dyestuff, and they were compared to the corresponding properties of the new inks that were prepared, both conventional and microemulsified. A significant improvement, mainly in the conductivity and particle size distribution, was concluded from a comparison of the new inks and the commercial inks, both conventional and microemulsified.

A. Kazlauciusas (Department of Colour Chemistry, University of Leeds) conducted the particle size and particle size distribution measurements.

References

1. Fryberg, M. *Rev Prog Color* 2005, 35, 1.
2. Georgiadou, K. L.; Tsatsaroni, E. G. *Dyes Pigments* 2001, 50, 93.
3. Georgiadou, K. L.; Tsatsaroni, E. G. *Dyes Pigments* 2002, 53, 73.
4. Georgiadou, K. L.; Tsatsaroni, E. G.; Kehayoglou, A. H. *J Appl Polym Sci* 2004, 92, 3479.
5. Eastman-Kodak. U.S. Pat. 6,136,079 (2000).
6. Fuji. U.S. Pat. 6,458,194 (2002).
7. Fuji. U.S. Pat. 6,582,502 (2003).
8. Annen, O.; Egli, R.; Hasler, R.; Henzi, B.; Jakob, H.; Matzinger, P. *Rev Prog Color* 1987, 17, 72.
9. Peters, A. T.; Gbadamosi, N. M. A. *Dyes Pigments* 1992, 18, 115.
10. Hallas, G. *J Soc Dyers Colourists* 1979, 95, 285.
11. Choi, J.-H.; Hong, S.-H.; Towns, A. D. *J Soc Dyers Colourists* 1999, 115, 32.
12. Holme, I. *Text Mag* 2004, 1, 11.
13. Kang, H. R. *J Imaging Sci Technol* 1991, 35, 189.
14. Magdassi, S.; Ben Moshe, M.; Berenstein, L.; Zaban, A. *J Imaging Sci Technol* 2003, 47, 357.
15. Zhong, Y. L.; Feng, J.; Chen, S. *Color Technol* 2005, 121, 76.
16. Peters, A. T.; Sener, M. E. *Dyes Pigments* 1987, 8, 99.
17. Griffiths, J. *Rev Prog Color* 1981, 11, 37.
18. Peters, A. T. *J Soc Dyers Colourists* 1988, 104, 344.
19. (a) Schulz, G. *Melliand Textilber* 2003, 83, 154; (b) Siegel, B.; Siemensmeyer, K.; Dorer, M. *Melliand Textilber* 1993, 79, 867.
20. Daplyn, S.; Lin, L. *Pigment Resin Technol* 2003, 32, 307.
21. Kipphan, H. *Handbook of Print Media*; Springer: Berlin, 2001.
22. Magdassi, S.; Ben Moshe, M. *Langmuir* 2003, 19, 939.