

Synthesis, Characterization and Application of Hetarylazo Disperse Colorants: Preparation and Properties of Ink-Jet Inks with a New Antimicrobial Agent for Ink-Jet Printing

E. K. Karanikas*, N. F. Nikolaidis

Department of Chemistry, Aristotle University, 541 24 Thessaloniki, Greece

DOI: [10.36348/sijcms.2021.v04i05.008](https://doi.org/10.36348/sijcms.2021.v04i05.008)

| Received: 18.05.2021 | Accepted: 24.06.2021 | Published: 26.06.2021

*Corresponding author: E. K. Karanikas

Abstract

The synthesis and characterization of two hetarylazo disperse colorants is described. These compounds were used for the preparation of ink-jet inks with and without active agents for digital printing. 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 which containing the new synthesized compounds with and without active agent were applied by exhaustion (dyed) on polyester and polyamide samples. Fastness (light, wash and rub) and also color properties of the samples were measured. Also, quantitative determination of the new antimicrobial agent was made from the dyed samples with exhaustion. The optimum application level required to give long lasting antimicrobial protection was determined by carrying out a series of antimicrobial testing.

Keywords: dyes/pigment, synthesis, antibacterial, polyhexamethylene bisguanidine, polyester, polyamide, cosmetotextiles.

Copyright © 2021 The Author(s): This is an open-access article distributed under the terms of the Creative Commons Attribution **4.0 International License (CC BY-NC 4.0)** which permits unrestricted use, distribution, and reproduction in any medium for non-commercial use provided the original author and source are credited.

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 [1].

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 non-aqueous 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 (eg. 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[2, 3].

Similar disperse colorants have been synthesized and used previously for the dyeing of cellulose acetate fibres. Preparation of analogous ink jet inks was also done and discussed [4].

Using heterocyclic dyes for ink-jet printing is a rather recent idea [1, 5-7]. Particularly dyes derived from benzothiazole-, benzisothiazole ring are advantageous with respect to their potential use as commercially competitive replacements on environmental and economic considerations for established anthraquinone dyes [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 fibre 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 hydrosulphit respectively [10]. Due to 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.

During the last decades there has been a growing popularity in the preparation of textile products with active agents as additives. Incorporating successfully an active ingredient (e.g. antimicrobial, fragrance) in a textile article is a challenge to the producer. It gives the possibility of producing innovative personalized finished articles reducing the production stages and minimizing waste water and energy consumption.

Among the numerous applications, there has been a growing interest in the development of bioactive textile materials with antimicrobial properties. Textile materials in contact with body provide the ideal environment for growth and multiplication of pathogenic microbes leading to objectionable odor, dermal infection, product deterioration, allergies and other related diseases. These factors necessitate the development of methods to impart antimicrobial resistance to textiles with all the usual desirable characteristics of textiles, as these textile materials find extensive use in different sectors related to healthy and hygienic life style apart from the conventional apparel usage. To be successful in the marketplace, these finishes should be durable and have selective activity towards undesirable organisms [11]. Use of such finishes will give to the finished article not only the desired colour design but additional properties which will increase the added value of the final article.

In continuation to our previous work on the synthesis of hetarylazo disperse dyes and preparation of ink-jet inks for polyester and polyamide printing two similar dyes was synthesized and characterized [4, 12-14]. These hetarylazo compounds I, II (Figure 1) were used for the preparation of water-based ink-jet inks with (formulations I.2, II.2) and without (formulations I.1, II.1) 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 [2, 15, 16]. The active ingredient used in this work was polyhexamethylene bisguanidine, a new antimicrobial agent known as GH-20. The same properties were measured for an ink with a commercially available disperse dye Disperse Blue 356 III (Figure 1) with and without the active ingredient.

The inks were used for dyeing to polyester and polyamide fabric. It was decided to apply the ink jet printing inks on polyester and polyamide by exhaustion in order to investigate whether 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.

Fastness properties of the printed samples were evaluated and color measurements and qualitative determination of the antimicrobial agent adsorbed on the samples were made. Also, an antimicrobial test on the printed polyester and polyamide samples with the active agent was made.

EXPERIMENTAL SECTION

Materials and methods

The following amines were commercially available and used without further purification: 6-Methoxy-2-aminobenzothiazole, 3-Amino-5-nitro [2, 1] benzisothiazole (Zhejiang, China). Commercial sample of CI Disperse Blue 356 III (Yorkshire Farben GmbH, Germany) was used as disperse dye (Figure 1). The commercially available dye Disperse Blue 356 (Yorkshire Colors, Germany) was used for comparison. Double-Jersey 100% polyester fabric white 190g/m² supplied by Greuter-Jersey AG (Switzerland) as well as nylon 6.6 (78F46, 1.69 dtexpf) supplied by KYKE HELLAS were used. Commercial grade 2-propanol (Fluka) and ethylene glycol (Riedel-de-Haen, Germany) were used. Alcoospers LFD (KYKE HELLAS SA) a condensation product of formaldehyde-sulphonic acid sodium salt was used as dispersing agent Polyhexamethylene bisguanidine PHMBG (commercial name GH-20) IV (Figure 1) was used as the antimicrobial agent.

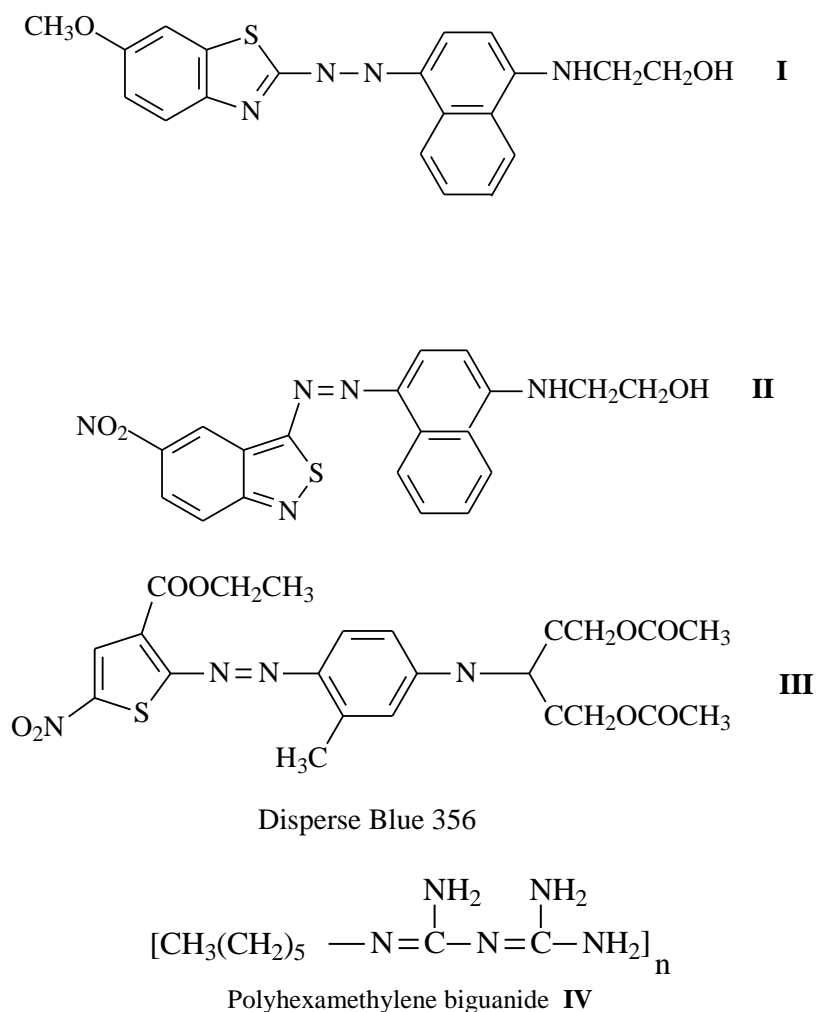


Fig-1: Structures of dyes I, II, III and the antimicrobial agent IV used.

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. ^1H -NMR data were obtained with a Bruker 300 AM spectrometer using $\text{CDCl}_3/\text{d}_6\text{-DMSO}$ 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 [12, 13]

These compounds were prepared by the diazotization of amines 6-Methoxy-2-aminobenzothiazole and 3-Amino-5-nitro [2, 1] benzoisothiazole followed by coupling with N-2-hydroxyethyl-1-naphthylamine.

Compound I

Yield of crude product 87.5%; purified by recrystallization (ethanol); m.p. 201–203 °C; λ_{max} (nm, CH_3OH): 561.0; ϵ_{max} ($\text{l mol}^{-1} \text{cm}^{-1}$, CH_3OH): 54,650; ^1H -NMR (δ , $\text{CDCl}_3/\text{d}_6\text{-DMSO}$): 3.26 broad s (1H, OH), 3.74 t (2H, H-b), 3.89 s (3H, CH_3O), 4.41 t (2H, H-c),

6.94 d (1H, H-20), 7.09 dd (1H, H-5), 7.29 d (1H, H-7) 7.50–7.76 m (3H, H-60-80), 7.86 d (1H, H-30), 7.96 d (1H, H-4), 8.08 d (1H, H-50); MS (m/e, %): 201.8 (8.3), 197.8 (12.2), 179.8 (83.3), 164.8 (81.4), 139.3 (25.1), 44.0 (100); Anal.(calc. found). C: 63.47, 62.80; H: 4.79, 4.72; N: 14.81, 14.24.

Compound II

Yield of crude product 97.9%; by column chromatography (silica gel, 10–90% ethyl acetate in toluene); m.p. 236–237°C; λ_{max} (nm, CH_3OH): 652.0; ϵ_{max} ($\text{l mol}^{-1} \text{cm}^{-1}$, CH_3OH):27700; ^1H -NMR (δ , $\text{CDCl}_3/\text{d}_6\text{-DMSO}$): 3.27 broad s (1H, OH), 3.82 t (2H, H-b), 4.49 t (2H, H-c), 6.82 d (1H, H-20), 7.53–7.71 m (3H, H-60–80), 8.09 d (1H, H-50), 8.16 d (1H, H-30), 8.44 d (1H, H-7), 8.88 dd (1H, H-6), 9.16 d (1H, H-4); MS (m/e, %): 393.8 (22.8, M^+), 186.1 (45.3), 90.1 (100), 60.1 (8.7), 45.0 (15.7); Anal. (calc. found). C: 58.00, 57.55; H: 3.84, 3.86; N: 17.80, 17.37.

Ink formulation

In Table 1 the water-based ink formulations containing 1% w/v dye, 75% v/v H_2O , a mixture of 2-propanol (IPA)/ethylene glycol (EG) 20/5 v/v as the miscible solvent, 0.05% w/v dispersing agent are given.

The mixture of ingredients was stirred for 10 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. The inks were filtered through a 1µm

filter to ensure their suitability for ink-jet printing. An amount 0.5 % v/v% of the active agent GH-20 was added in the inks prepared using a Sonicator UP100H (Hilscher). In table 1 the reference formulations (without active agent) are also included.

Table-1: Disperse ink formulations

Formulation	Dye%(w/v)	H ₂ O%(v/v)	IPA%(v/v)	EG% (v/v)	Alcoospers%(w/v)	GH-20 %(v/v)
I.1	1	75	20	5	0.05	-
I.2	1	75	20	5	0.05	0.5
II.1	1	75	20	5	0.05	-
II.2	1	75	20	5	0.05	0.5
III.1	1	75	20	5	0.05	-
III.2	1	75	20	5	0.05	0.5

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, California, USA); 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, 90 days.

Dyeing

Dyeing was carried out in a Rotadyer dyeing machine (John Jeffreys Ltd, Rochdale Banbury, UK) with a depth of dyeing 2% o.m.f. in a liquor ratio of 1: 20, pH 4 achieved with a buffer CH₃COOH-CH₃COONa. The dyeing process is given in Figure 2 for the polyester and polyamide dyeing respectively (Figure 2).

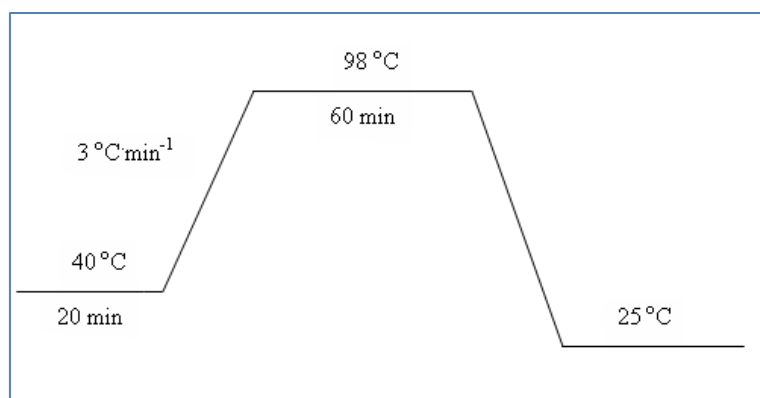


Fig-2: Dyeing process of polyester and polyamide

After treatment of the dyed fibres with PHMBG

The active agent PHMBG was applied with aftertreatment of the dyed samples at temperature 40°C, pH 4.8 with a depth of dyeing 0.5% o.m.f. in a liquor ratio 1:20 for 30min. Exhaustion values were calculated by measuring spectrophotometrically the absorbance of the compound at its λ_{\max} = 193,4nm in the initial bath and the bath after treatment using the equation:

$$E_{\%} = \frac{(A_0 - A_t)}{A_0} \times 100, \text{ where:}$$

A_0 : initial bath absorbance at λ_{\max}

A_t : bath absorbance at λ_{\max} at time t

Fastness tests

Wash fastness of the prints was carried out according to ISO 105 C02, light fastness was carried out according to ISO 105 B02 whereas rub fastness ISO 105 X12 [17].

Color measurements

The reflectance values of the prints was measured using a Macbeth Color Eye 3000 spectrometer (Williamston, S. Carolina, USA) under D65 illumination, 10 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 λ_{\max} .

Quantitative antibacterial assessment of the printed sample treated with PHMBG

This was done according to ISO 20743:2007 as follows:

1. A piece of the sample was placed into a container with a lid.
2. A 0.2ml inoculum of *Staphylococcus aureus* was placed in microdroplets on the surface of the sample. 0.05% Tween 80 was added to the inoculum as a wetting agent.
3. The specimen was incubated 18h at 37°C.
4. 20ml of Lethen broth was added to the container and shaken. The bacteria in the liquid were quantified by using a series of dilution plates.

RESULTS AND DISCUSSION

The compounds I, II were synthesized by coupling a diazotised heteroarylamine with N-2-hydroxyethyl-1-naphthylamine (Figure 1) [12, 13, 18]. Heteroaromatic amines were selected as diazocomponents because the heterocyclic ring is a powerful electron-withdrawing residue. Derivatives of isothiazole, i.e. heterocyclic systems containing sulphur as the π -excessive heteroatom, represent a very electronegative diazo component, thus having a strong bathochromic effect, perhaps due to the d-orbitals of sulphur atom [19, 20]. Thus isothiazole ring systems are particularly useful for providing blue dyes. Coupling with a benzene ring such as in I (Figure 1) an intense violet 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, 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 2-6.

1. Surface tension measurement

Inks for application via inkjet printing should have a surface tension in the range of 21-48 or 30-60 mNm⁻¹ [21, 22]. It can be seen from figure 3 that all the inks prepared had a surface tension within the operational range with a slight increase over the relevant period of time. All inks prepared have surface tension values within the proposed ranges. The stability of the surface tension over a period of 90 days shows that all inks prepared are suitable to be used as ink-jet inks. The addition of GH-20 does not influence the surface tension and despite a slight increase surface tension values lie within the acceptable limits. This slight increase in surface tension can be attributed to the higher surface activity conferred by the phenolic hydroxyl groups with the hydrophobic character. When surface tension increases is a benefit for the adhesional wetting of the ink. Surface values are in the acceptable range for ink-jet inks [22, 23] in all cases (commercial and new synthesized dyes) remaining satisfactorily stable. Surface tension values of the inks containing the new synthesized inks were lower than those of the inks with the commercial dye. This is in favour of their adhesion wettability (Figure 3).

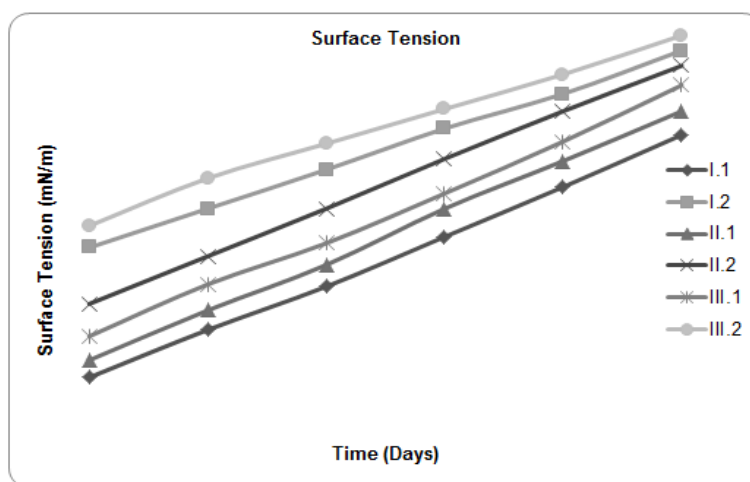


Fig-3: Plots of surface tension values vs. time for the ink formulations with and without the active agent the inks containing the commercial dye with and without active agent

2. Viscosity measurement

It is generally accepted that ink jet inks should have a viscosity lower than 2cP [23] although it is not unknown for such inks to have a viscosity lower than 3cP [24]. The corresponding formulations with antimicrobial agent presented lower viscosity values with the same curve shape. Both inks with and without the active agent showed a sharp increase in viscosity.

This sharp increase in viscosity can be attributed to the presence of the dispersing agent, Alcosperse LFD, which is a sodium salt of a polysulphonated derivative full dissociation of which produce more anionic repulsions and thus causing an increment in viscosity during the storage time [2]. Viscosity curves shape is similar for the inks with both commercial and new synthesized dyes: both of them are increasing during the

period of the time storage. However viscosity values of all dye preparations are unacceptably high for ink-jet

inks [22, 23], while the acceptable operational range for ink-jet inks is 2-3cP (Figure 4).

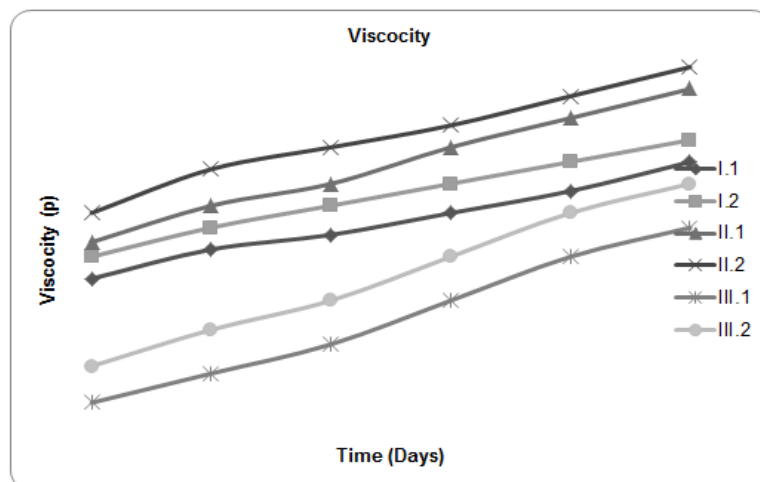


Fig-4: Plots of viscosity values vs. time for the ink formulations with and without the active agent the inks containing the commercial dye with and without active agent

3. Conductivity measurement

Conductivity values of the prepared inks are given in Figure 5. Dispersing agent and colorant structure affects 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.

Conductivity values of the commercial dye ink preparations are significantly lower (120.2-241 $\mu\text{S}/\text{cm}$) than the corresponding hetarylazo dyes preparations (164.8 -599 $\mu\text{S}/\text{cm}$). However both ink preparations with the new hetarylazo ink preparations are in the acceptable range values compared with the commercial ones (Figure 5).

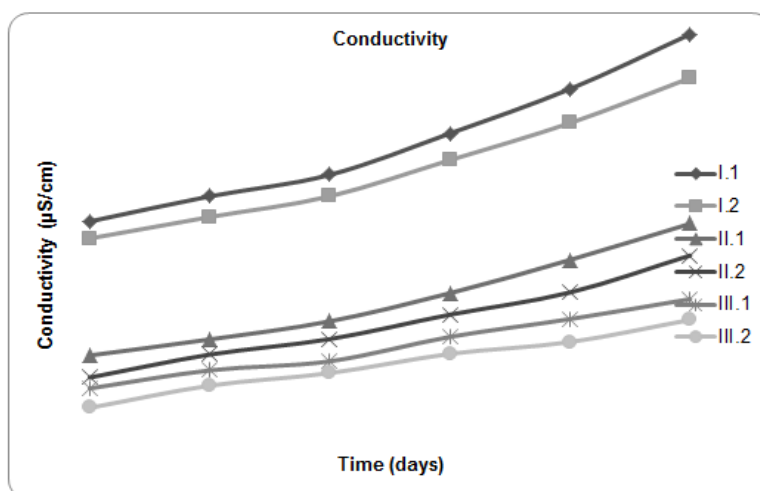


Fig-5: Plots of conductivity values vs. time for the ink formulations with and without the active agent the inks containing the commercial dye with and without active agent

4. pH measurement

The composition of the dispersion determines the pH (Figure 6). Apparently, due to the acetylation of the ionisable hydroxy groups, ink 1 has the highest pH value, although remaining lower than the acceptable neutral region for ink-jet printing [16]. In this case pH correction with a buffer solution is necessary to use them as ink jet inks. Contrarily pH values of the inks with the compounds I, II, references or/and with the

active agent present lower pH values (3-4) compared with the corresponding of the commercial dye (4.6-3.8). In both cases pH values are unacceptable for ink-jet inks and a pH correction is necessary (Figure 6).

Addition of antimicrobial agent results in an increasing in pH values in both cases (ink I.2 and ink II.2) remaining though still not acceptable (Figure 6).

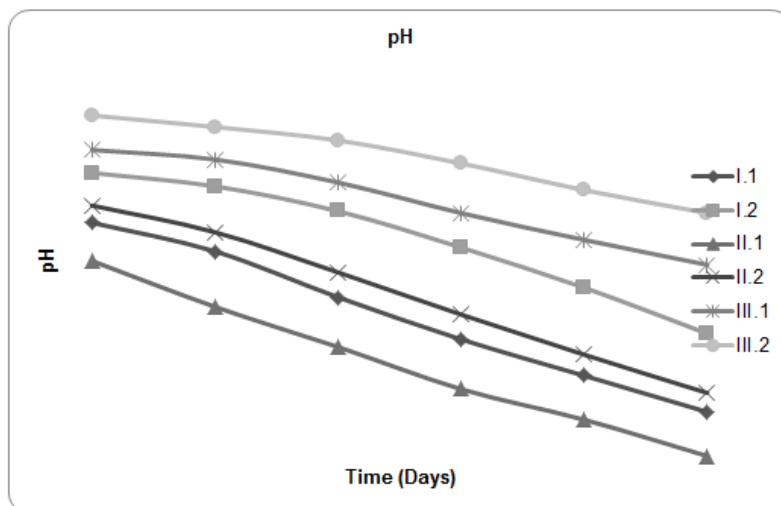


Fig-6: Plots of pH values vs. time for the ink formulations with and without the active agent the inks containing the commercial dye with and without active agent

Color measurement

Table 2 shows the relevant colorimetric data and color strength values for the prints after reduction clearing. From table 2 the following are concluded:

The presence of antimicrobial agent (formulations I.2, II.2) does not result practically in a differentiation in K/S values of the samples. The

samples dyed with the formulations I.1, I.2 (inks containing the benzothiazole compound I) with h values between (300.20° and 325.20°) are in the dark blue area ($270-360^\circ$) in the color circle while the samples dyed with the formulations II.1, II.2 containing the benzoisothiazole compound II are in the green-blue color circle area ($180-270^\circ$). This was also visually confirmed.

Table-2: Colorimetric data of the dyed samples

Sample	Fibre	λ_{max}	K/S	L*	a*	b*	C*	h°
I.1	PES	540	5.06	39.64	20.90	-14.98	25.71	324.38
I.2	PES	540	5.11	39.32	20.15	-14.01	24.54	325.20
II.1	PES	640	7.58	36.94	-7.15	-12.76	14.63	240.73
II.2	PES	640	7.11	37.31	-7.16	-12.73	14.61	240.65
I.1	PA	580	3.67	46.95	2.096	-36.02	41.68	300.20
I.2	PA	580	4.06	49.64	2.090	-36.98	40.71	301.38
II.1	PA	680	4.59	49.24	-9.26	-6.10	11.09	213.38
II.2	PA	680	4.86	48.58	-9.59	-6.18	11.41	212.80

Fastness properties of the dyed samples

The fastness data obtained for the dyed samples are given in Table 3. The staining of the wool, polyester and acrylic fibres in the multifibre strip were found to be from good to excellent in all cases. Color change was quite good for polyamide samples with Compound I, good for polyester samples with Compound I and excellent in all cases for Compound II. As it was expected the man-made less hydrophilic fibres such as nylon and acetate were stained more by both disperse dyes. The natural fibre cotton with a medium hydrophilicity was also stained, while staining of wool with the highest hydrophilicity was very good (samples PES II.1 and II.2) to excellent as it was expected. All dyeings on polyester fabric for both inks with or without the inclusion of the active agent present

average light fastness (3-4 on blue scale, Table 3). Rub fastness both wet and dry were medium, (3-4 on grey scale) for both polyester printed samples with and without active agent. Rub fastness both wet and dry were medium to excellent for all polyamide samples. However, the light fastness on polyamide were low (2 on blue scale). It is well known that disperse dyes are mainly used for the dyeing and printing of polyester fibres and to a lesser extent for the dyeing and printing of nylon where they show moderate build up and fastness properties [25]. These results are in agreement with previous experimental findings for the same dyes and can be attributed to their structural features in connection to the substrate [26]. Once again the inclusion of the active agents does not affect the light fastness of the polyamide dyeings.

Table-3: Fastness properties of the dyed samples

Sample	Fibre	Colour Change	Wash Fastness						Light Fastness	Rub Fastness	
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool		Dry	Wet
I.1	PES	4	4	3-4	3	4-5	5	5	3-4	4	3
I.2	PES	4	4	3-4	3	4-5	5	5	3-4	4	3
II.1	PES	5	5	4-5	3	4	5	4-5	3-4	3	3
II.2	PES	5	5	4-5	3	4	5	4-5	3-4	3	3
I.1	PA	3-4	4	3-4	3	4-5	5	5	2	4	3
I.2	PA	3-4	4	3-4	3	4-5	5	5	2	4	3
II.1	PA	5	3-4	5	3-4	5	5	5	2	5	4
II.2	PA	5	3-4	5	3-4	5	5	5	2	5	4

Antibacterial measurements of the printed samples

The antibacterial activity was tested against a negative gram bacterial klebsiella pneumonia. The

antibacterial agent PHMBG showed high levels of antibacterial activity as this is expressed by the high values % bacterial area reduction in Table 4.

Table-4: Quantitative antibacterial assessment of polyester and polyamide samples treated with PHMBG

Quantitative Assessment of Activity-ISO 20743: 2007 K. pneumoniae		
Fibre	Dye	% Reduction
Polyester (PES)	Compound I	99.9%
Polyamide (PA)	Compound I	82.9%

After 20 washes

Quantitative Assessment of Activity-ISO 20743: 2007 K. pneumoniae		
Fibre	Dye	% Reduction
Polyester (PES)	Compound I	90.5%
Polyamide (PA)	Compound I	62.3%

The bacterial free area is approaching almost 100% of the treated area for k. pneumoniae for the polyester substrate. The same test was performed after 20 washings with excellent results (% reduction of k. pneumoniae 94.5%) indicating that PHMBG is not eliminated from the substrate after repeated wet treatments thus fulfilling the requirements of an antibacterial additive.

Determination of the PHMBG from the dyed samples

Table 5 shows the exhaustion values of the dyed polyester and polyamide samples after treated with PHMBG. This amount is responsible for the antimicrobial protection activity of the dyed samples.

Table-5: Exhaustion values of PHMBG after treatment of the dyed samples.

Fibre	Dye	E% (dyed)
Polyester (PES)	Compound I	73.08
Polyester (PES)	Compound II	72.24
Polyamide (PA)	Compound I	60.61
Polyamide (PA)	Compound II	59.03

CONCLUSIONS

Two hetarylazo disperse colorants were synthesized by diazotization of 6-Methoxy-2-aminobenzothiazole and 3-Amino-5-nitro[2, 1] benzoisothiazole and coupling with substituted N-2-hydroxyethyl-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.

The synthesised dyes were used for the preparation of ink-jet inks by adding antimicrobial

agent as an active agent. 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. All the prepared inks with the synthesized dyes were applied by exhaustion to polyester and polyamide fabric.

The inclusion of active ingredients in the ink formulations allows the production of specialised 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.

Fastness properties of the printed samples were evaluated and colour measurements were made. Quantitative determination of the active agent adsorbed on the polyester and polyamide fibre was also made by UV-Vis spectrophotometer. The antibacterial activity of the samples treated with PHMBG as well as their stability against wet treatments was assessed and found to be excellent.

ACKNOWLEDGEMENTS

This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Reinforcement of Postdoctoral Researchers - 2nd Cycle” (MIS-5033021), implemented by the State Scholarships Foundation (IKY).

REFERENCES

1. Fryberg, M. (2005). Dyes for ink-jet printing. *Review Progress Coloration*, 35(1), 1-30.
2. Kang, H. R. (1991). Water based ink jet ink. II. Characterization. *Journal Imaging Science Technology*, 35, 189-194.
3. Yamanoto, T., Haruta, M., Koike, S., Shiota, K., Yoshihira, A., & Suzuki M. (1997). Textile printing method, printed textile obtained thereby, and ink. U.S. Patent, no. 8910720.
4. Cosolia, C. T. & Tsatsaroni, E. G. (2010). Synthesis and Characterization of Hetarylazo Disperse Colorants: Preparation and Properties of Conventional and Microemulsified Inks for Polyester Ink-Jet Printing. *Journal Applied Polymer Science*, 116 (3), 1422-1427.
5. Eastman-Kodak. (2000). U.S. Patent, no 6136079.
6. Fuji. (2002). U.S. Patent, no 6458194.
7. Fuji. (2003). U.S. Patent no 6582502.
8. Annen, O., Egli, R., Hasler, R., Henzi, B., Jakob, H. & Matzinger, P. (1987). Replacement of disperse anthraquinone dyes. *Review of Progress in Coloration and Related Topics*, 17(1), 72-85.
9. Peters, A.T. & Gbadamosi, N.M.A. (1992). 5, 6-(6,7-)Dichlorobenzo thiazolylazo dyes for synthetic-polymer fibres. *Dyes & Pigments*, 18(2), 115-123.
10. Choi, J.-H., Hong, S.-H. & Towns, A. D. (1999). Azobenzene disperse dyes-past development and future prospects. *Journal Society Dyers Colorists*, 115 (1), 32-37.
11. Yang, Y., Corcoran, L., Vorlicek, K. & Li, S. (2000). *Text Chem. Color Am Dyestuff Rep*, 32(4), 48-54.
12. Georgiadou, K. L., & Tsatsaroni, E. G. (2002). Hetarylazo disperse dyes derived from substituted N, N-bis- β -hydroxy- and N, N-bis- β -acetoxy-ethylaniline. *Dyes & Pigments*, 53(1), 73-78.
13. Georgiadou, K. L., Tsatsaroni, E. G. & Kehayoglou, A. H. (2004). Synthesis and Characterization of Hetarylazo Disperse Dyes Derived from Substituted N-Acetoxyethylanilines—Application on Cellulose Acetate. *Journal Applied Polymer Science*, 92 (6), 3479-3483.
14. Kosolia, C. T., Tsatsaroni, E. G., & Nikolaidis, N. F. (2011). Disperse Ink-jet Inks: Properties and Application to Polyester Fibres. *Coloration Technology*, 127(6), 357-364, doi: 10.1111/j.1478-4408.2011.00334.x.
15. Daplin, S., & Lin, L. (2003). Evaluation of pigmented ink formulations for jet printing onto textile fabrics. *Pigment and Resin Technology*, 32(5), 307-318.
16. Holme, I. (2004). Digital ink jet printing of textiles. *Textile Magazine*, 1, 11-16.
17. *Methods of Test for Colour Fastness of Textiles and Leather*. (1990). Bradford: Society of Dyers and Colourists.
18. Peters, A. T., & Sener, M. E. (1987). Disperse Dyes Derived from 4-Phenylazo-1-naphthylamine and 4-Phenylazo-5-hydroxy-1-naphthylamine. *Dyes & Pigments*, 8(2), 99-118.
19. Hallas, G. J. (1979). The Effects of Terminal Groups in 4-Aminoazobenzene and Disperse Dyes Related Thereto. *Journal of the Society of Dyers and Colourists*, 95(8), 285-294.
20. Griffiths, J. (1981). Recent Developments in the Colour and Constitution of Organic Dyes. *Review Progress Coloration*, 11(1), 37-57.
21. Schulz, G. (2003). *Melliand Textilberichte*, 83(3), 154-159.
22. Siegel, B., Siemensmeyer, K., & Dorer, M. (1993). *Melliand Textilberichte*, 79(11/12), 864-865.
23. Daplin, S., & Lin, L. (2003). Evaluation of pigmented ink formulations for jet printing onto textile fabrics. *Pigment and Resin Technology*, 32(5), 307-318.
24. Kipphan, H. (2001). *Handbook of Print Media*; Springer: Germany.
25. Burkinshaw, S. M. (1995). *Chemical Principles of Synthetic Fibre Dyeing*. Chapman & Hall, London, UK.
26. Broadbent, A. D. (2001). *The basic principles of textile coloration*. Dyers Company Publication, West Yorkshire.