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Original Research Article

Ink-Jet Inks with UV-Absorber Tinuvin 327 as Active Agent for Polyester and Polyamide Digital Printing

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Abstract

UV-absorber Tinuvin 327 was used as active agent in this work. It was added in three different amounts (0.25% 0.5% and 1.0%) in water-based disperse ink-jet inks. The surface tension, pH, viscosity and conductivity of the prepared formulations were monitored over a period of 90 days in order to estimate the ink stability and the compatibility of the UV-absorbers with the ink constituents. The inks were used for ink-jet printing on paper, transfer printing on polyester and polyamide and thermostabilization. Wash light and rub fastness were evaluated on the printed samples. Color coordinates were measured. Qualitative determination of the active agents, adsorbed on the printed samples was made by using UV-Vis Spectroscopy.

Key words: ink-jet ink, UV-absorber, digital printing, polyester, polyamide.

INTRODUCTION

UV-absorbers have been utilized to protect polymeric materials from photodegradation caused by sunlight or ultra-violet rich artificial light. Recently, interest has developed in the application of UV-absorbers in the dyeing and printing of textile materials to protect their color from fading. High light fastness of dyed/printed materials is important especially for automobile colored upholstery, which can be exposed to direct sunlight and temperatures above 50°C.

Various commercial UV-absorbers, mainly of the benzophenone and Benzotriazole and less of other classes (benzoic acid esters, hindered amines) used directly for polyester, woo1, polyamide and polypropylene fibres caused a light fastness improvement ranging from 0 to 2 units of the blue standard scale for various dyes [1-3].

Ink-jet printing is one of the fastest growing of imaging technologies; showing benefits over the conventional printing methods of roller and flatbed screen printing. These benefits include economic production of small runs, just in time delivery, quick response to fashion demands, no stock holding of chemicals and printed fabrics, no chemical waste, as well as low energy and water consumption [4].

In this study UV-absorber Tinuvin 327 was used as active agent. The aim of this work is the preparation of stable disperses ink jet inks for digital printing applications with and without UV-absorbers. Physicochemical properties of the inks pH, conductivity, surface tension and viscosity were studied. The inks were used for digital ink jet printing to polyester and polyamide samples. Fastness properties and colorimetric coordinates of the prints are also performed.

MATERIALS AND METHODS

Double-Jersey 100% polyester fabric white 190g/m^2 supplied by Grenter-Jersey AG (Switzerland) as well as nylon 6.6 (78F46, 1.69 dtexpf) supplied by KYKE HELLAS were used. The dye CI Disperse Blue 60 kindly supplied by Yorkshire Colors, Germany was used as a disperse dye (Figure 1). 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. Tinuvin 327 (Figure 1) was the UV-absorber.

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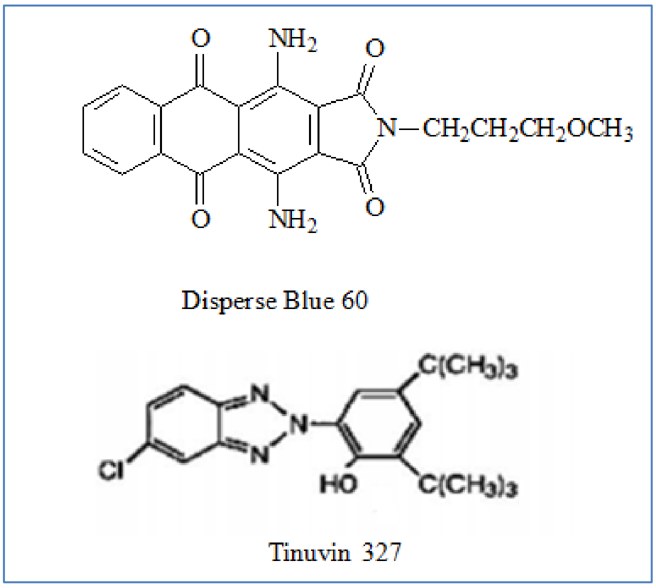

Fig-1: Structure of the dye and the UV-absorber used

Ink formulation

The ink formulations contain 2% 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 and 0.25%, 0.5% and 1% of UV-absorber Tinuvin 327. The mixture of ingredients was homogenized for 10 min using a Sonicator UP100H homogenizer at room temperature.

Table-1: Disperse ink formulations

Formulation	Dye/ %(w/v)	H_2O/ %(v/v)	IPA/ %(v/v)	EG/ % (v/v)	Alcoospers/ %(w/v)	Tinuvin 327/ % (w/v)
1.1	2	75	20	5	0.05	-
1.2	2	75	20	5	0.05	0.25
1.3	2	75	20	5	0.05	0.5
1.4	2	75	20	5	0.05	1.0

Surface tension conductivity, viscosity and pH measurements

Surface tension measurements were made using a KSV Sigma 70 tensiometer fitted with a De Nouy platinum ring. Conductivity measurements were performed using a Crison Conductimeter Basic 30 and pH measurements were made using a WTW Microprocessor 535 pH meter, viscosity measurements were made using a Viscostar plus+ H (Fungilab) viscometer. The above properties were measured at room temperature and atmospheric pressure for 1, 7, 14, 30, 60 and 90 days for all the inks.

Ink-jet printing

Printing was performed on paper, with a Canon iP7250 printer, followed by transfer printing on paper and then thermostabilization to polyester and polyamide fabric for 30 sec.

The printed samples were then rinsed in cold water and reduction cleared using a solution comprising 2g/l sodium dithionite and 1.5g/l sodium carbonate at 60^{o} C in a liquor ratio of 20:1 for 20 min. The reduction cleared samples were rinsed in cold water and allowed to dry in the open air.

Fastness tests

Wash fastness of the prints was carried out according to BS1006:1990CO2 test, light fastness was carried out according to BS1006:1990BO2 test, whereas dry and wet rub fastness was carried out according to ISO 105 X12[5].

Color measurements

The reflectance values of the prints were measured using a Macbeth CE 3000 spectrometer under D65 illumination, 10 standard observer with UV and specular component included. The CIE1976 L*a*b*C* h^{o} coordinates and the K/S values were calculated from the reflectance values at the appropriate λmax.

Identification and determination of the UV-absorber adsorbed on the printed samples

Quantitative determination of the UV-absorber of the printed sample was made after extraction of the two active agents with polyethylene glycol 200 and measuring spectrophotometrically the extract at 343nm (λmax of Tinuvin 327). Four extraction cycles (1g sample in a liquor ratio 1:10, 30min, $130^{o}C$ for polyester and $98^{o}C$ for polyamide) were carried out for the quantitative recovery of the active agent from the fabric.

RESULTS AND DISCUSSION

Physical Properties of the Inks

Figure 2 shows the pH values of the inks against time of storage. From the above figures can be concluded that the blue formulation without active agent has slightly acid pH. This is due to the fact that the blue dye has been milled and processed in acid environment. The addition of the UV-absorber Tinuvin 327 in the formulations causes decrease in pH values compared to the reference formulation, followed by small decrease over the period of storage time which is proportional. This can be explained that the active agent has acid character due to the phenyl group which contain in their molecules. The inks with the active agents are approaching the neutral region. Given that acceptable pH values for ink-jet inks are near the neutral region (6.5 -8.0) all the formulations need correction with buffer solution.

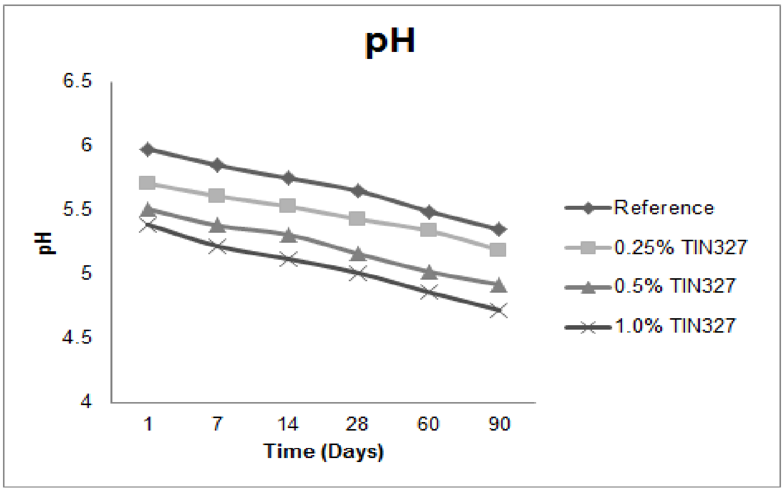

Fig-2: Plots of pH values vs time for the ink formulations

Figure 3 shows the effect of storage time on the conductivity of the inks. The presence of Tinuvin 327 increases conductivity values compared to the reference ink which already presents high conductivity values. This can possible be attributed to the presence of ionized hydroxy group which may give rise to higher conductivity values compared to the reference ink. Conductivity values are also proportional to the quantity of the agent used in both dye inks prepared.

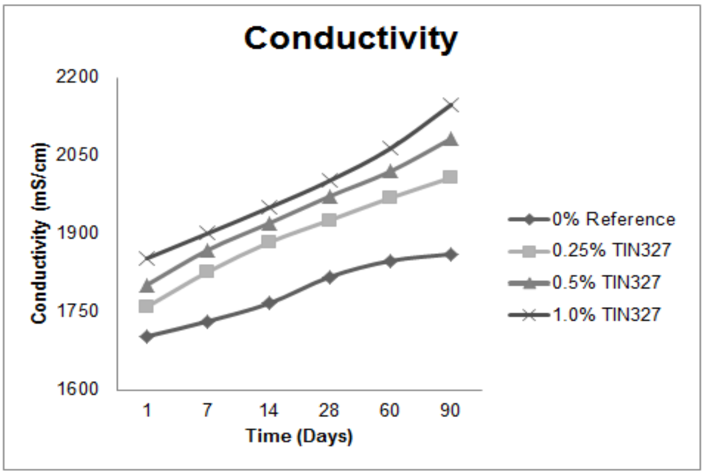

Fig-3: Plots of conductivity values vs time for the ink formulations

Figure 4 shows the surface tension values of the inks prepared against storage time. All the surface tension values are increasing during the time storage. The addition of the active agent causes a normal increase until the end of the measurements. This increase in surface tension which becomes sharper can be attributed to the higher surface activity conferred by the long hydrophobic chains of Tinuvin 327. Surface tension increase is at the benefit of the adhesional wetting of the ink. Typical surface tension values of commercial ink-jet inks for textile printing are in range 21-48 or 30-60 mNm^{-1}[4,8]. The surface tension values of all inks prepared with and without the additives are in the acceptance range making them suitable for ink jet applications.

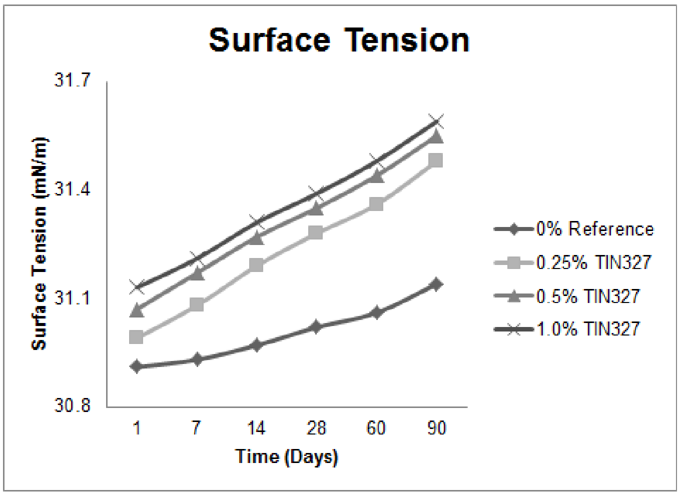

Fig-4: Plots of surface tension values vs time for the ink formulations

Figure 5 shows the effect of storage time on viscosity. It is generally accepted that ink-jet inks should have a viscosity lower than 2cP to be suitable for digital printing application although it is not so strange for such inks to have a viscosity up to 3cP[6]. All inks with and without the active agents showed an intitial sharp increase in viscosity during the period of storage. This sharp increase can be attributed to the presence of the dispersing agent present in all inks, Alcosperse LFD, which is a sodium salt of a polysulphonated derivative full dissociation of which produce more anionic repulsions and thus causing an increase in viscosity as a function of storage time.

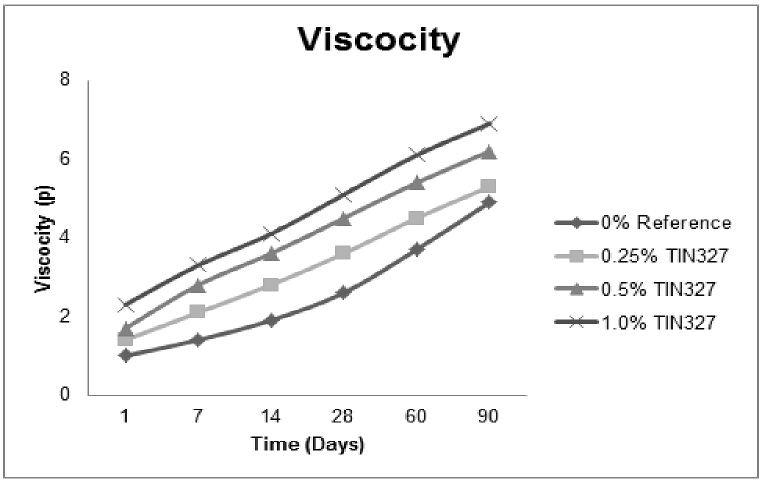

Fig-5: Pl-ots of viscosity values vs time for the ink formulations

Fastness properties

The wash light and rub fastness properties of the digitally printed polyester and polyamide samples are given in Table 2. The wash fastness for all printed samples after the reduction clearing treatment performed is excellent with no staining of the adjacent fibres of the multifibre strip (values 5) and no color change of the digitally printed samples (values 5). Rub fastness both wet and dry were excellent, (5 on grey scale) for both polyester printed samples with and without active agent.

Light fastness of the reference printed polyester (value 4-5) was medium, while reference polyamide sample presented a low (value 2) light fastness value. Addition of the UV-absorber in the ink formulations resulted, in almost all cases, an improvement in light fastness with range 0.5-1.5 units on the blue standard scale. Comparing the effectiveness on the light fastness of the two UV-absorbers, it is evident that the UV-absorber had good effects. However, the addition higher amount of active agent caused an improvement in light fastness (samples 1.3, 1.4). Finally Table 2 showed that the light fastness on polyester were higher, due to the fact that disperse dyes are used especially for polyester dyeing and printing.

Table-2: Fastness values of the printed samples

Sample	Fibre	Colour Change	Wash Fastness						Light Fastness	Rub Fastness	
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool		Dry	Wet
1.1	PES	5	5	5	5	5	5	5	4-5	5	5
1.2	PES	5	5	5	5	5	5	5	5	5	5
1.3	PES	5	5	5	5	5	5	5	5-6	5	5
1.4	PES	5	5	5	5	5	5	5	6	5	5
1.1	PA	5	5	5	5	5	5	5	2	5	5
1.2	PA	5	5	5	5	5	5	5	2-3	5	5
1.3	PA	5	5	5	5	5	5	5	3	5	5
1.4	PA	5	5	5	5	5	5	5	3-4	5	5

Color measurements of digitally printed samples

The ink formulations were applied to polyester and polyamide fibres by transfer printing followed by thermostabilization. Almost 100% transfer of the printed ink from the paper to the textile substrate is taking place under the transfer conditions employed. It is believed that the transfer of the ink from the paper to the textile substrate is being made not through a conventional sublimation transfer mechanism but through a melt or wet transfer mechanism where a thin layer from the digitally printed paper is being deposited on the polyester or polyamide substrate.

Table 3 shows the relevant colorimetric data and color strength values for the polyester and polyamide printings. The presence of the active ingredient in the digital ink formulation has resulted in a significant dye increase as this is expressed by the higher K/S values of the polyester prints containing Tinuvin 327 compared to the reference.

The active ingredients, may be capable to form hydrogen bonds between their hydroxy group and the amine groups or the N-heteroatom of the disperse blue dye respectively and thus increasing the solubility of the sparingly soluble disperse dye in the aqueous face and thus possibly acting as a "carrier", promoting higher dye uptake by the polyester and polyamide fibre compared to the reference digital printing ink. This higher uptake was especially noticed with the bigger and bulkier blue disperse dye which possess two free amine groups and a long aliphatic chain in the molecule making the dye bulkier and more difficult to penetrate the rigid polyester fibre [7].

On polyamide application the inclusion of the active agents has the same effect as on polyester. The color strength of the polyamide prints is lower compared to polyester ones and this can be explained that disperse dyes are used for polyester dyeing and printing, where they show good build up and to a lesser extent for polyamide application[8].

The h^o values of the prints both on polyester and polyamide are in the green-blue region of the color circle.

Table-3: Color coordinates L*, a*, b*, C*, h^o and color strength K/S values of the printings

Sample	Fibre	λmax	K/S	L*	a*	b*	C*	h^o
1.1	PES	680nm	0.255	83.45	-7.77	-5.91	9.76	217.25
1.2	PES	680nm	0.504	85.40	-10.58	0.42	10.58	187.75
1.3	PES	680nm	0.860	83.26	-12.55	-1.42	12.63	186.44
1.4	PES	680nm	1.460	76.53	-20.08	-13.77	24.34	214.44
1.1	PA	680nm	0.145	82.54	-1.76	0.18	1.77	174.27
1.2	PA	680nm	0.300	86.82	-12.83	-4.84	13.73	200.64
1.3	PA	680nm	0.480	89.48	-12.38	-3.72	12. 90	196.78
1.4	PA	680nm	0.580	79.95	-19.45	-13.96	23.94	215.67

Determination of the UV-abs from the digitally printed samples

Table 4 shows the amounts of UV-absorber extracted from the printed polyester and polyamide samples after four extraction cycles with polyethylene glycol 200 as a solvent. The extracted amount of active agent show that about 20% of active agent UV-absorber over mass of fabric is deposited by the digital printing head on the textile substrate. This amount is responsible for the UV protection activity of the digitally printed samples.

Table-4: Amount (mg/L) of Tinuvin 327 adsorbed on printed samples

	POLYESTER	**POLYAMIDE**
Tinuvin 327-DW % w/v	**AMOUNT mg/L**	**AMOUNT mg/L**
0.25	213	88
0.5	308	123
1.0	398	193

CONCLUSIONS

UV-absorber Tinuvin 327 was used for digital printing on paper and transfer to polyester and polyamide fabrics. The physical properties pH, surface tension, conductivity and viscosity of the inks were monitored over a period of 90 days. Color, wash, rub and light fastness measurements of the prints were made and presented. Quantitative determination of the two agents adsorbed on the fibre was also made and the results regarding the UV protection activity of the textiles were excellent. Addition of the UV-absorber in the ink formulations resulted an improvement in light fastness. Comparing the effectiveness on the light fastness of the UV- absorber, it is evident that had good results on the printed samples.

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