

Research Article

Preparation of Ink-Jet Inks with Quinizarin as “Antifraud Marker” for Textile Digital Printing

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Abstract: Quinizarin, an anthraquinone derivative, was used as “antifraud marker”. It was added in three several amounts (0.25%, 0.5% and 1.0%) in water-based disperse ink-jet inks. Surface tension, viscosity, conductivity and pH of the ink formulations were monitored over a period of 90 days in order to estimate the ink stability and the compatibility of the “antifraud” active agents with the ink constituents. The inks were used for ink-jet printing to polyester and polyamide samples. Fastness (light, wash and rub) and also color properties of the samples were measured. Finally, qualitative and quantitative determination of the active agent was made from the printed samples with extraction.

Keywords: Anti-fraud markers, digital printing, disperse dyes, ink-jet inks, Quinizarin.

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INTRODUCTION

Ink jet printing is one of the fastest growing of imaging technologies; compared to conventional printing methods, ink jet printing generates lower waste and uses lower amounts of energy and water [1-3].

Ink jet inks must be carefully formulated to yield specific properties that enable optimum droplet formation within the fine nozzles of a printing head for application at high speed. Such properties are dependent upon the pH, surface tension, viscosity, conductivity and particle size distribution of the ink. Furthermore, inks designed for the ink-jet printing of textile materials need to satisfy various fastness criteria namely wash, light and rubbing [2-4].

Water-based ink-jet inks offer environmental advantages over their non-aqueous based counterparts, through reduced emissions of volatile organic compounds that are otherwise present in solvent-based formulations. With environmental considerations continuing to have ever-greater impact upon industry and legislation, textile producers have to carefully examine 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 a monohydric alcohol (methanol, ethanol, isopropanol), 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 [4-5].

The increasing use of CAD systems, with the consequent ability to store patterns in digital form, makes it particularly attractive [6]. Additionally, the use of electronic method of carrying out the printing operation and thereby eliminate the costly and time-consuming process of screen-making is of great importance in terms of drastically reducing the production cost [7]. With the increased pressure from developing textile markets in the Far East, the textile printer in Europe, Japan and the USA must respond with both increased quality and shorter response time. This means supplying new design concepts, sample and production of printed fabrics in a wide range of color ways in a time frame unheard of a few years ago and with substantially reduced production cost.

Conventional printing is growing in the Far East and is declining in the developed Western printing markets whereas digital textile printing is growing fast in the old established developed textile markets such as of Europe, Japan and USA [8].

Since 1991, digital textile printing systems have been available that can be used for proofing and small sample production. A considerable number of major research projects (Europe, Japan, USA) aimed at taking digital textile printing to full production scale [9].

It is common to everyone that developed countries are flooded with cheap low quality counterfeit products which try to copy well established brand names. This occurs for all industrial products from garments, textiles and household items, to electric appliances etc. The competition is unfair because years of research and development to market new products, new designs and fashionable items are wasted along with huge financial loss due to dramatic drop of sales. This has a catastrophic influence in the industry in the economies of the developed countries leading to higher unemployment and factory closures.

Many organic compounds have been used conventionally as antifraud tracers and markers. 1,4-Dihydroxyanthraquinone, commercially named Quinizarin or Solvent Orange 86, is an organic compound derived from anthraquinone. Quinizarin is an orange or red-brown crystalline powder. It is formally derived from anthraquinone by replacement of two hydrogen atoms by hydroxyl (OH) groups. It is one of ten dihydroxyanthraquinone isomers and occurs in small amounts (as a glycoside) in the root of the madder plant, *Rubia tinctorum* [10]. Quinizarin is an inexpensive dye that is used to color gasoline and some heating oils. It is used as an intermediate for the synthesis of indanthrene- and alizarin-derived dyes. The OH groups can be replaced by chloride. Chlorination and bromination afford other dyes. Amination (replacement of one OH by ArNH) with aniline derivatives followed by sulfonation affords other dyes such as Acid Violet 43. It is also used to

form lake pigments with calcium, barium, and lead [11].

The present research work aims to develop an easy to use “antifraud digital printing system” to distinguish the original from the counterfeit items. The “antifraud digital printing” ideally should be able to print on a variety of substrates such as natural and synthetic textiles, paper and packaging material, glass etc. The “antifraud digitally printed” material will be easily distinguished from the counterfeit printed product. Quinizarin was used as antifraud marker (Figure-1). Three different amounts of Solvent Orange 86 were added in the water-based disperse ink-jet inks prepared. The inks were used for ink-jet printing of polyester and polyamide samples. Fastness and color properties of the samples were measured. Qualitative and quantitative determination of Quinizarin desorbed from the printed samples was made and a simple spectrophotometrical method for their detection was proposed.

EXPERIMENTAL SECTION

Materials

Double-Jersey 100% polyester fabric white 190g/m² supplied by Greter-Jersey AG (Switzerland) as well as nylon 6.6 (78F46, 1.69 dtexpf) supplied by KYKE HELLAS were used. Commercial samples of C.I Disperse Blue 60 (Serilene Brilliant Blue 2GN) were kindly supplied by Yorkshire Colours, Germany (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. Anthraquinone derivative Quinizarin (Solvent Orange 86) (KYKE HELLAS SA) was used as antifraud tracer (Figure-1).

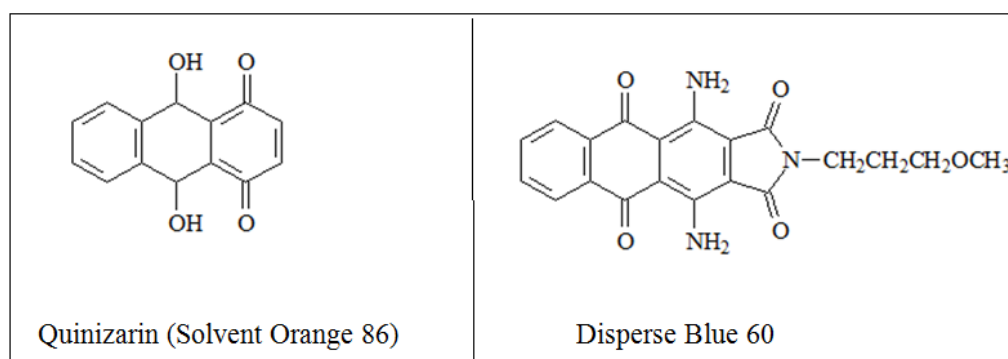


Fig-1: The active agent and the Dye used

Ink Formulation

In Table-1 the water-based ink formulations containing 2% w/v dye, 75% v/v H₂O, a mixture of 2-propanol (IPA)/ethylene glycol (EG) 20/5 v/v as the miscible solvent, 0.05% w/v dispersing agent [12, 13]

and various % amounts of solution 0.25% w/v Quinizarin in solvent butoxy ethanol, as active agent are given. The reference formulations without the inclusion of the 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)	Alcoopers/%(w/v)	0.25% Quinizarin(w/v)/ %(v/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

The mixture of ingredients was homogenized for 10 min using a Sonicator UP50H (Hilscher) homogenizer at room temperature.

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, 28, 60, 90 days for the inks with and without active agent.

Ink-Jet Printing

Printing was performed on paper, with printer Canon iP7250, followed by transfer printing on paper and then transfer and thermostabilization at 190°C 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° 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.

Fastness Tests

The fastness of polyester and polyamide prints were carried out according to ISO 105 C02 (washing), ISO 105 B02 (light) and ISO 105 X12 (rubbing) [12].

Color measurements

The reflectance values of the prints were measured using a Macbeth CE 3000 spectrometer under D65 illumination, 10° standard observer with UV included and specular component excluded. The CIE L*a*b*C*H* coordinates and the K/S values were calculated from the reflectance values at the appropriate λ_{max} (680nm in case of Disperse Blue 60).

Identification and quantitative determination of the active agent adsorbed on printed polyester and polyamide samples

Quantitative determination of the active agent on the printed sample was made after extraction of Quinizarin with a mixture of cresol/heavy naftha 50/50 v/v as the extract solvent, and measuring spectrophotometrically the extract at 483.5nm (λ_{max} of Solvent Orange). One extraction cycle (0.4g sample in a liquor ratio 1:25, 30min, at room temperature for both polyester and polyamide) were carried out for the quantitative recovery of Quinizarin from the printed polyester and polyamide fabrics. Figure 2 and 3 show the spectrum of Quinizarin (Solvent Dye 86) and Disperse Blue 60.

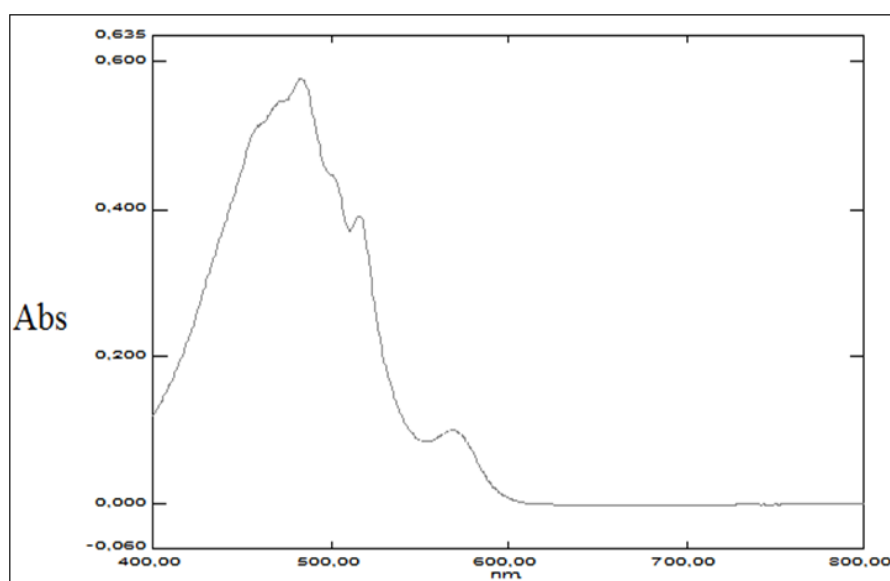


Fig-2: The spectrum of Solvent Orange 86 used

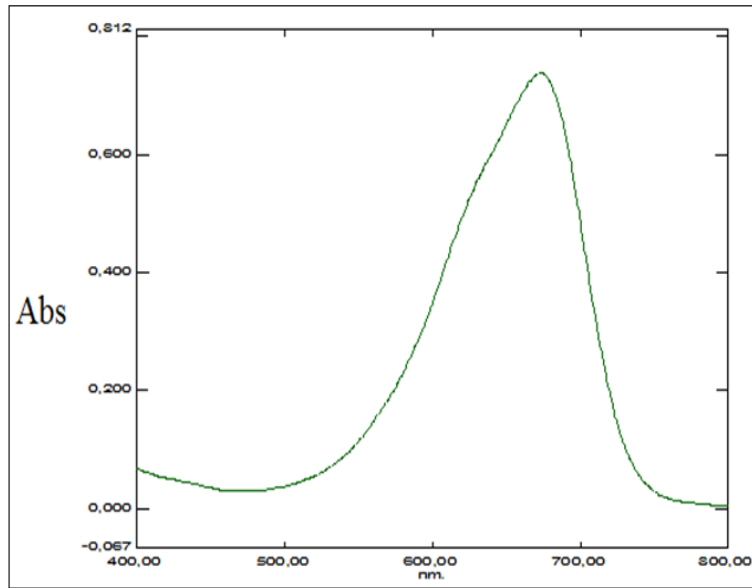


Fig-3: The spectrum of Disperse Blue 60 used

RESULTS AND DISCUSSION

Ink Properties Measurement

Three water-based ink-jet inks with dye Disperse blue 60 containing quinizarin as antifraud marker were prepared (Table-1). One reference ink-jet ink (without antifraud agent) was also prepared. Monitoring a formulation over a period of time is a widely accepted method for evaluating dispersion stability [4, 8, 13]. In this study the surface tension, pH, viscosity and conductivity of the formulations prepared were monitored over a period of 90 days.

pH Measurement

Figure-2 shows the pH values of the inks prepared with and without the active agent against time of storage. From above figures it can be concluded that

all formulations have generally low values pH (5.98-5) followed by small decrease over the period of storage time. This is due to the fact that the blue dye has been milled and processed in low pH. The addition of the antifraud agent in the blue dye formulation results in a pH decrease in all cases compared to the reference formulation (without antifraud agent). This can be explained by the fact that the solution of quinizarin has acid pH in the region of 4.5- 5 due to its phenolic character and when added to the blue formulation inks causes a slightly drop in the pH of the resulting formulation. Given that acceptable pH values for ink-jet inks are near the neutral region (6.5-8) [14, 15] all the blue formulations with and without the active agent need a slightly correction with a buffer solution.

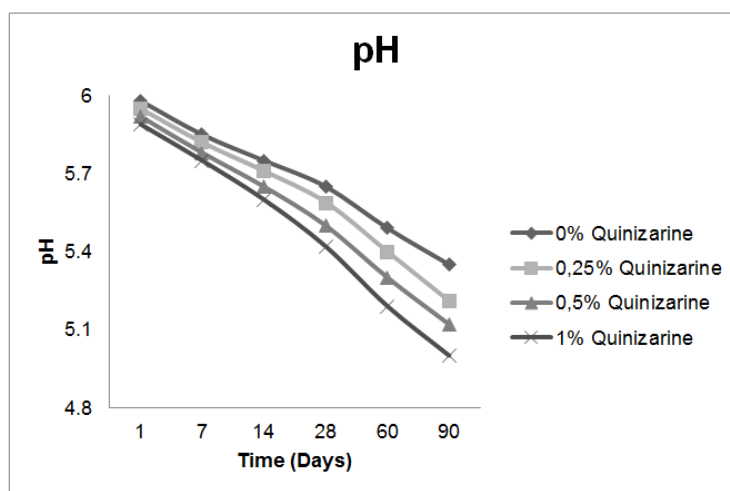


Fig-4: Effect of storage time on pH for Disperse Blue 60 inks with and without the active agent

Conductivity Measurement

Figure-3 shows the effect of storage time on the conductivity of the blue inks. It can be seen that the

presence of antifraud marker in all cases causes an increase in conductivity values compared to the reference formulations. This can be attributed to the

presence of ionized phenolic hydroxyl groups of quinizarin which may give rise to higher conductivity values compared to the reference blue ink. Conductivity

values are also proportional to the quantity of the agent used in both dye inks prepared.

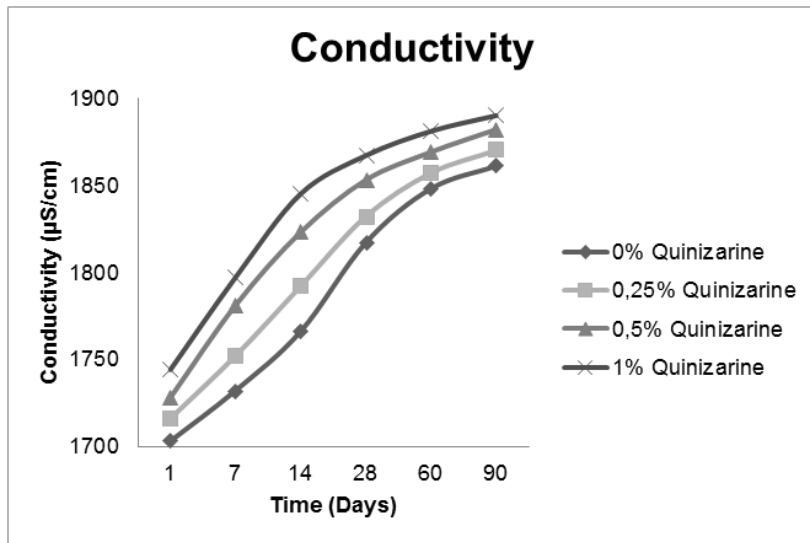


Fig-5: Effect of storage time on the conductivity of Disperse Blue 60 inks with and without the active agent

Surface Tension Measurement

Figure-6 shows the surface tension values of a small increase during the storage time. It is widely accepted that typical surface tension values of commercial ink-jet inks for textile printing are in the range 21-48 or 30-60 mNm⁻¹ [14, 15]. 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 tracer 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.

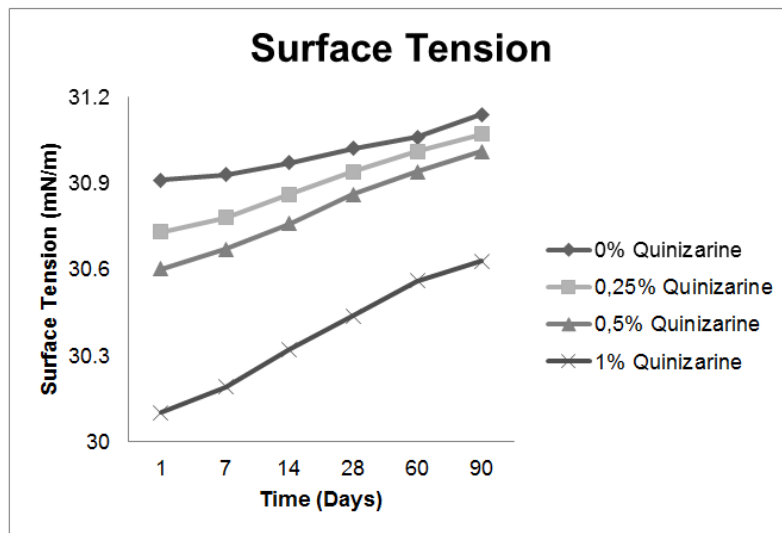


Fig-6: Effect of storage time on the surface tension of Disperse Blue 60 inks with and without the active agent

Viscosity Measurement

Figure-7 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 unknown for such inks to have a viscosity up to 3cP [14-15]. Both blue inks with and without the active agent showed a

slightly increase in viscosity followed by a sharp increase in viscosity after about 28 days of storage. 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. All prepared inks with and without the active agents show acceptable viscosity values up to 28 days of storage for ink jet ink applications for digital printing [16]. Finally the inks

which contain the antifraud marker have upper viscosity values due to the presence of ionized phenolic hydroxyl groups of quinizarin which may give rise to higher viscosity values compared to the reference blue ink.

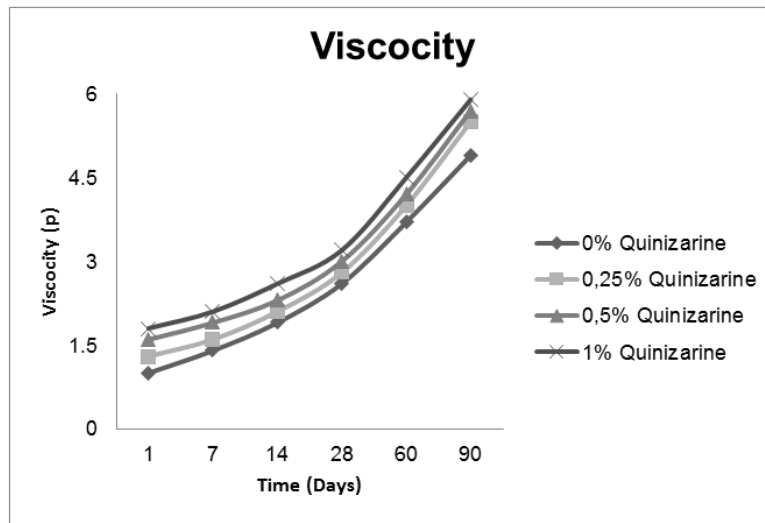


Fig-7: Effect of storage time on the viscosity of Disperse Blue 60 inks with and without the active agent

Ink-jet printing of polyester and polyamide fabrics Fastness properties of the prints

Tables 2 & 3 show the fastness and color properties of the ink jet inks applied to polyester and

polyamide after a storage period of 90 days with and without the inclusion of the tracer.

Table-2: Fastness properties 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	4-5	5	5
1.3	PES	5	5	5	5	5	5	5	4-5	5	5
1.4	PES	5	5	5	5	5	5	5	4-5	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	5	5
1.3	PA	5	5	5	5	5	5	5	2	5	5
1.4	PA	5	5	5	5	5	5	5	2	5	5

Table-2 shows that addition of Quinizarin does not affect the light fastness properties of the polyester and polyamide prints and this confirms the fact that the active agents show good compatibility with the dyes and the other ingredients of the ink formulations. All prints on polyester fabric for both inks with or without the inclusion of the active agent present average light fastness (4-5 on blue scale, Table-2) and excellent wash fastness (5 on grey scale) for both color change and staining of the adjacent fibres. Rub fastness both wet and dry were excellent, (5 on grey scale) for both polyester printed samples with and without active agent.

On polyamide application wash fastness was excellent (5 on grey scale), as in the case of polyester application, for both ink-jet inks with or without the inclusion of the active agent. Rub fastness both wet and dry were excellent, (5 on grey scale) for all polyamide

printed 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 [16]. 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 [17]. Once again the inclusion of the active agents does not affect the light fastness of the polyamide prints.

Color Measurement

Table-3, shows the color coordinates L*, a*, b*, C*, H* and the color strength, K/S values, of the polyester and polyamide prints with and without the inclusion of the active agent. A significant increase in the K/S values for all blue ink-jet ink has been observed

on polyester application with the inclusion of the active agents. It seems that the agent has a “carrier action” on polyester application [18]. On polyamide application the inclusion of the active agent seems to have the same effect as on polyester. The color strength of the

polyamide prints are much lower compared to polyester ones and this can be explained that disperse dyes are used especially for polyester dyeing and printing of where they show good build up and a lesser extent for polyamide application [16].

Table-3: Colorimetric data of the dyed samples

Sample	Fibre	λ_{max}	K/S	L*	a*	b*	C*	h°
1.1	PES	680nm	0.255	83.45	-7.77	-5.91	9.76	217.25
1.2	PES	680nm	0.32	82.44	-9.49	-7.81	12.29	219.45
1.3	PES	680nm	0.353	82.16	-10.36	-8.66	13.50	219.22
1.4	PES	680nm	0.379	81.45	-10.62	-9.11	13.99	220.61
1.1	PA	680nm	0.145	82.54	-1.76	0.18	1.77	174.27
1.2	PA	680nm	0.169	82.56	-3.38	-1	3.52	196.45
1.3	PA	680nm	0.175	81.83	-2.98	-0.79	3.09	194.86
1.4	PA	680nm	0.189	81.56	-3.28	-0.94	3.42	196

With negative a* and b* values and h° = 174.27-220.61° the blue polyester and polyamide printings lie in the blue-green sector of the color circle.

Identification and quantitative determination of the active agents adsorbed on printed polyester and polyamide sample

The effect of Quinizarin on the thermofixed fabric was evident since effect of the printed fabric was able to be seen by bare eye on suitable light cabinet conditions. This result could be related to the property of the active agent to increase the surface tension of the corresponding inks (Figure 6). Since printing involves superficial adhesion of the ink on the fabric and not penetration in the fibre (dyeing) this surface tension increase is at the benefit of the adhesional wetting of the ink [19]. Similar results were obtained with the addition of other active agents in the digital printing inks such as antimicrobials which from the same water system “transferred” to the substrate (PES, PA) with the same application method paper to fabric (unpublished

results). 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. Almost 100% transfer of the printed ink from the paper to the textile substrate is taking place under the transfer conditions employed.

Quantitative determination of the tracer Quinizarin included in the ink-jet ink formulation was performed. The quantitative determination was made on the printed samples after extraction of the active agent with a mixture of cresol/heavy naphtha 50/50 v/v and measuring spectrophotometrically the extract at 483.5nm (λ_{max} of Quinizarin). Table-4 summarize the results obtained for polyester and polyamide samples printed with various amounts of the active agent.

Table-4: Amount (mg/L) of Quinizarine extracted from polyester (PES) and polyamide (PA) printed samples

POLYESTER		POLYAMIDE	
Sample	Amount mg/L	Sample	Amount mg/L
1.2	20.69	1.2	16.48
1.3	38.58	1.3	29.81
1.4	73.26	1.4	66.37

The desorption of active agents is generally more for the higher application levels of the active agents but not proportionally. It seems that an application level of 0.25% in the ink-jet ink printing formulation is enough and can easily be detected in the solution after extraction with a mixture of cresol/heavy naphtha at room temperature for 30 minutes as it was described in the experimental section. The above results indicate that Quinizarine can be used in the ink-jet ink printing formulation as “marker” to distinguish for example between the original and imitation articles.

CONCLUSIONS

The use of Quinizarin as active agent in the formulation of ink-jet inks for digital printing has been studied. The active agent can be used as “marker” in the printing paste in order to detect original from counterfeit products.

A simple spectrophotometrical method is described which allows an easy and accurate detection of the active agent and thus allows the use of active agent as antifraud marker. The above method provides a simple and on the spot quick, reliable and inexpensive laboratory method for distinguishing the counterfeit products.

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