BIO-BASED PIGMENT INKS FOR INKJET PRINTING APPLICATIONS

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1. INTRODUCTION

The textile printing industry is undergoing a significant transition from traditional techniques to digital ones, highlighted in major global exhibitions such as ITMA 2023 (Milan, Italy), Techtextil 2024 (Frankfurt, Germany), and FESPA 2024 (Amsterdam, Netherlands). A key trend is the growing market demand for inkjet printing using pigment inks. This process offers substantial sustainable advantages over traditional dye-based printing methods, such as reactive or acid inks, which require pre-treatments with urea and post-steaming and washing treatments, with consequently higher environmental impacts.

It is reported that textile industries all over the globe produce and use approximately 1.3 million tons of dyes and pigments [1]. Unfortunately, many of these synthetic dyestuffs, auxiliaries, and dyeing wastes, predominantly fossil based, pose a significant threat to human health and the environment. Inkjet printing is the cleanest textile method, but the dyestuffs and auxiliaries used still represent an environmental risk. Inkjet printing with natural dyes or pigments is a novel process with unparalleled ecological characteristics [2]. However, the market still lacks commercially available inkjet inks with bio-based pigments.

Natural dyes, particularly those derived from plants, display a few inherent drawbacks, such as low affinity for the textiles, poor colour fastness, a limited range of colours, low yields, low shades reproducibility, long extraction processes, seasonal variation, and low shelf life [3]. Bacterial fermentation to produce colouring agents is promising, but still limited. Scaling up the production of microbial pigments is accompanied by several difficulties; however, recent technological developments have helped to partially overcome these [4]. Recent advances include the production of nature-based pigments from (bacterial) fermentation followed by chemical routes using bio-based components [5], and methods where colour-producing bacteria grow directly on textiles, simultaneously printing them and creating unique patterns [6] [7].

So far, bio-based pigments have been applied mainly by conventional processes, leaving a need to introduce them in inkjet printing. This work describes the development of bio-based inkjet printing pigment inks, namely water-based textile inks suitable for piezoelectric printheads with bio-based pigments from bacterial fermentation.

2. MATERIALS AND METHODS

2.1 Materials

The textile textiles used were a cotton-based (99% cotton, 1% elastane, 150 g/m^2) and a polyester-based (100% polyester, 150 g/m^2) fabrics, supplied by RIOPELE (Portugal). The polymers used in the pre-treatments were a biopolymer based on a cationic polysaccharide (Biopolymer 2), and a polymer dispersion based on non-ionic aliphatic polycarbonate-polyether polyurethane (Binder A). The pigments used were indigo (blue) and quinacridone (red), supplied by PILI (France) in powder form, and obtained by bacterial fermentation.

2.2 Methods

Pre-treatment: textiles were pre-treated using foulard impregnation with the polymers described in the section 2.1, followed by a drying process at 100ºC for 3 minutes.

Inks formulation: a synthetic biodegradable binder, a crosslinking agent, distilled water, a hygroscopic agent, wetting agents, an anti-foam agent, and the pigment were mixed at room temperature. Indigo pigment was used in 0.1%, 0.5% and 1%, added either directly as powder or as a pre-dispersion. The red pigment was used in 0.5% in powder form. Then the formulation was sonicated (in an ice bath), followed by filtration using a 5 µm cellulose filter.

Indigo pre-dispersion: indigo pigment was mixed with surfactants (dispersing and wetting agents) and dispersed in a ball mill (PM100 planetary ball mill by Retsch, Germany) at 350 rpm, using 3 mm diameter zirconia balls, over 5, 8, 15 or 115 hours.

Characterization: the physical properties of the inks were analysed as follows - viscosity (smart series rotational viscosimeter by Fungilab, Spain), density (calculated dividing the mass by volume), surface tension (pendant drop method in the optical tensiometer Theta Flex by Biolin Scientific, Finland), particle size (Zetasizer NanoSeries Nano ZS90 by Malvern, UK).

Printing: the pre-treated textile fabrics were printed using two inkjet printing technologies, either with valve jet printhead (Chromojet from Zimmer) or piezoelectric printhead (Kyocera KJ4B-Z), with a native resolution of 1200 dpi. Once printed, the samples were dried at 100 ºC for 3 minutes, followed by thermofixation at 150 ºC for 5 minutes.

Printing characterization: the printed fabrics were characterized regarding their colour fastness to washing (domestic washing at 40 ºC, 20 cycles), to artificial light (ISO 105-B02:2014) and to rubbing (ISO 105-X12:2016).

3. RESULTS AND DISCUSSION

3.1 Chromojet printing

For the Chromojet printing application, two inks were developed using 0.5% of indigo and 0.5% of quinacridone pigments used in powder form, and their properties are shown in Table 1. The inks meet the requirements of the Chromojet equipment. The indigo ink presented a slight agglomeration and sedimentation in the bottle, while the quinacridone pigment dispersed very well in the water-based formulation and no sedimentation was observed.

Table 1. Properties of the inks developed with indigo and quinacridone pigments in powder form

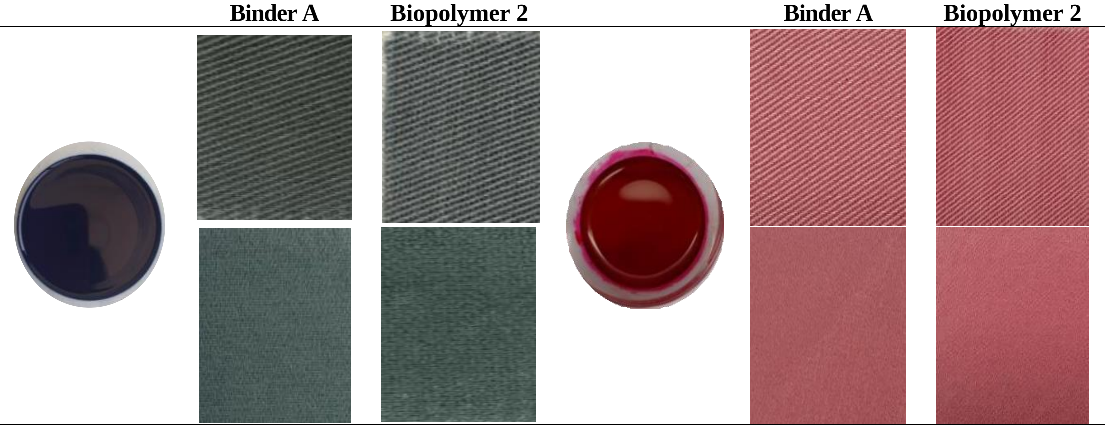
Ink properties	0.5% indigo	0.5% quinacridone
Viscosity (cP)	7.89 @ 22 °C (60 rpm)	6.81 @ 22 °C (100 rpm)
Density (g/cm^3)	1.07	0.93
Surface Tension (dynes/cm^2)	34.6	31.3
Particle size	200 - 350 nm[a]	< 5 µm

[a] Measured in a water dispersion at 0.075% of pigment, due to a limitation of the equipment.

Table 2 and Table 3 show a summary of the main achievements on the application of the bio-based inks applied using Chromojet printing.

Table 2. Indigo and red inks (pigments in powder form) and the result of their application on textile fabrics

		Indigo ink			Red ink	
		Binder A	Biopolymer 2		Binder A	Biopolymer 2
Cotton						
Polyester						



All samples showed a good colour intensity. However, the textile samples printed with indigo exhibited higher colour intensity when pre-treated with Binder A, while the red printed samples had a slightly more intense colour when pre-treated with Biopolymer 2. Overall, the red pigment exhibited very good colour fastness, showing significantly better results when compared to indigo. Indigo pigment also showed good colour fastness to rubbing (>3), while both pigments exhibited excellent colour fastness to light (>4). Up to 10 washing cycles, indigo ink printed on cotton pretreated with Biopolymer 2 and on polyester pretreated with Binder A displayed acceptable colour fastness to washing (≥3).

Table 3. Colour fastness properties of inkjet-printed (Chromojet) textile samples with 0.5% indigo and 0.5% red inks (grey scale evaluation) for two pre-treatments: Binder A and Biopolymer 2

		Cotton				Polyester			
		Binder A		Biopolymer 2		Binder A		Biopolymer 2	
Indigo ink	Washing[a]	3, 2-3, 2-3, 2-3, 2-3		3-4, 3, 3, 2-3, 2-3		4-4, 4-5, 4, 2-3, 2-3		3, 3, 2-3, 2-3, 2-3	
	Rubbing	Dry 3-4	Dry 3-4	Dry 4-5	Wet 3-4	Dry 3-4	Wet 3-4	Dry 4	Wet 3-4
	Artificial light	> 4		> 4		> 4		> 4	
Red ink	Washing[a]	5, 4-5, 4-5, 4, 3-4		5, 4-5, 4-5, 4, 3-4		5, 4-5, 4-5, 4, 3-4		4-5, 4, 4, 3-4, 3	
	Rubbing	Dry 4-5	Dry 4-5	Dry 4-5	Wet 4	Dry 4	Wet 4	Dry 3	Wet 2
	Artificial light	> 5		> 5		> 5		> 5	

[a] Results presented for 1, 5, 10, 15 and 20 washing cycles at 40 ºC.

3.2 Piezoelectric printheads

As piezoelectric printheads have more restricted particle size requirements than Chromojet, and given the results previously obtained, the indigo was pre-dispersed in a ball mill prior to its addition to the ink formulation. Different milling times were tested, and the best results (improved dispersion, leading to lower agglomeration in the ink formulation) were obtained with 115 hours in the mill. Inks with different concentrations of indigo were then prepared (0.1% and 1%) and their properties are shown in Table 4. These fulfil the requirements of the piezoelectric printhead.

Table 4. Properties of the inks developed with indigo pigment pre-dispersed for 115 hours in the ball mill

Ink properties	0.1% indigo ink	1% indigo ink
Viscosity (cP)	5.27 @ 22 °C (60 rpm)	6.33 @ 22 °C (100 rpm)
Density (g/cm^3)	0.99	0.96
Surface Tension (dynes/cm^2)	32.3	32.3
Particle size	< 5 µm	< 5 µm

Overall, the 1% indigo ink applied using a piezoelectric printhead showed better results than the other inks, revealing greater intensity, colour depth, and design definition (Table 5). Despite the slight sedimentation of the pigment (not shown), it was easily overcome by shaking the bottle, and the nozzles of the printhead did not clog.

In this case, all samples pretreated with Biopolymer 2 demonstrated better colour fastness to washing compared to Binder A, with very promising results (≥3 after 20 cycles). Colour fastness to rubbing and light showed excellent performance across all printing applications, as summarized in Table 6.

Table 5. Textile printed samples with indigo inks (0.1%, 1%) using pre-dispersed indigo (115 h in the mill)

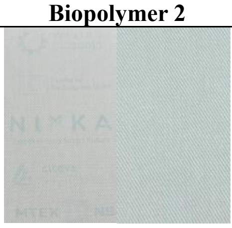
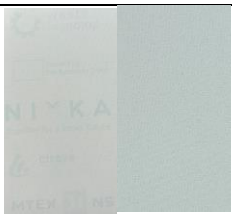
	0.1% indigo		1% indigo	
	Binder A	**Biopolymer 2**	**Binder A**	**Biopolymer 2**
Cotton				
Polyester			N/A	

Table 6. Colour fastness properties of inkjet-printed samples (piezoelectric printhead) with 0.1% indigo ink (gray scale evaluation) for two pre-treatments: Binder A and Biopolymer 2

		Cotton				Polyester			
		Binder A		Biopolymer 2		Binder A		Biopolymer 2	
Indigo ink	Washing[a]	3, 2, 1-2, 1-2, 1		4, 4, 3-4, 3-4, 3		4, 3-4, 3, 3, 3		4, 4, 4, 4, 4	
	Rubbing	Dry 4-5	Wet 4	Dry 4-5	Wet 4-5	Dry 4-5	Wet 4	Dry 4-5	Wet 4-5
	Artificial light	> 4		> 4		> 5		> 5	

[a] Results presented for 1, 5, 10, 15 and 20 washing cycles at 40 ºC.

4. CONCLUSION

This study highlights the significant potential of bacterial fermentation pigments as sustainable materials for bio-based inks for inkjet printing on cotton and polyester textiles. It also shows that biopolymers can be used as efficient pre-treatments to improve the print properties. These findings pave the way for innovative applications in the fashion industry and print-on-demand, offering an eco-friendly alternative to traditional printing methods.

5. ACKNOWLEDGEMENT

This work was carried out under the Waste2BioComp project - Converting organic waste into sustainable bio-based components, GA 101058654, funded under the topic HORIZON-CL4-2021-TWIN-TRANSITION-01-05 of the Horizon Europe 2021 – 2027 programme.

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