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Digital Printing Knitted Fabrics made of Polyamide, Cotton and Blends thereof

Digitalni tisk poliamida in mešanic bombaž-poliamid

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Abstract

Knitted fabrics with different compositions, i.e. 100% cotton (CO), 100% polyamide (PA), and a blend of 50% cotton and 50% polyamide (CO/PA), were digitally printed with reactive dyes. The cotton fabric was pretreated with a conventional alkaline solution of alginate thickener, sodium carbonate and urea. The polyamide fabric was pretreated with an acidic solution of galactomannan thickener. The CO/PA blend was pretreated once with the alginate and once with the galactomannan preparation. The aim of the study was to determine whether the proposed preparation is suitable for printing polyamide with reactive dyes and which preparation is more suitable for printing the cotton-polyamide blend. The CIE $L^*a^*b^*$ colour values, the colour depth (K/S) and the dye penetration of the printed samples were compared. It was determined that under the same printing conditions, the highest colour depth was achieved on cotton, while a lower depth was recorded on polyamide. The colour depth on the cotton-polyamide blend was lower than on the two pure fabrics. For some colours, the colour depth was higher with the alginate thickener preparation, for others with the galactomannan thickener, so that no definitive preference for one preparation over the other can be given for printing blends. The colour fastness of the prints to dry rubbing (crock test), light and washing at 40 °C was acceptable for all samples.

Keywords: digital printing, reactive dyes, polyamide, cotton, preparations

Izvleček

Pletivo z različno surovinsko sestavo: 100-odstotni bombaž (CO), 100-odstotni poliamid (PA) in mešanica 50 % bombaža in 50 % poliamida (CO/PA) je bilo digitalno tiskano z reaktivnimi barvili. Bombažno blago je bilo pred tiskanjem impregnirano s alkalno raztopino alginatnega zgostila, natrijevega karbonata in sečnine. Poliamidno blago je bilo impregnirano s kislno raztopino galaktomananskega zgostila. Mešanica CO/PA je bila impregnirana ali z alginatno ali z galaktomanansko apreturo. Namen raziskave je bil ugotoviti, ali je predlagana apretura primerna za digitalno tiskanje poliamida z reaktivnimi barvili in katera apretura je bolj primerna za tiskanje mešanice iz bombaža in poliamida. Na vzorcih, potiskanih s cian, magenta, rumeno in črno, so bili izmerjeni CIE $L^*a^*b^*$ barvne vrednosti, globina barvnih tonov (K/S) in pretisk barvila na hrbtno stran blaga. Ugotovljeno je bilo, da se pri istih pogojih tiskanja dosežejo najvišje K/S vrednosti na bombažu in nižje na poliamidu. Globina barve na mešanicah je bila nižja kot na obeh čistih pletivih. Za nekatere barve so bile K/S -vrednosti višje ob impregnaciji z alginatnim zgostilom, za nekatere



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z galaktomananskim zgostilom, tako da za nobeno apreturo ne moremo reči, da je primernejša za tiskanje mešanic bombaž/poliamid. Barvne obstojnosti tiskov na suho drgnjenje (crock test), svetlobo in pranje pri 40 °C so bile ustrezne pri vseh vzorcih.

Ključne besede: digitalni tisk, reaktivna barvila, poliamid, bombaž, mešanica, impregnacija

1 Introduction

Digital printing is the latest, but already fully established textile printing technology. Dyes in the form of tiny droplets of dye solutions (ink) are sprayed onto the fabric through numerous micrometre-sized nozzles [1].

Reactive, disperse, acid and pigment dyes in the form of ink are used for digital textile printing. The dyes must match the textile substrate, bond physically and chemically with the fibres, fix sufficiently and have the required fastness properties.

Reactive dyes are a group of dyes with brilliant shades and good fastness properties that chemically bind to textile fibres. They are most commonly used for printing on cellulose fibres and are also suitable for printing on silk, wool and polyamide [2]. They are anionic, as one or more sulphonate groups are bound to the dye molecule (dye-SO₃⁻). Reactive dyes can bind to the hydroxyl groups of cellulose via the reactive system and form covalent bonds under alkaline conditions, usually through nucleophilic bimolecular substitution or nucleophilic addition mechanisms [3]. Reactive dyes also react with water molecules, a process known as hydrolysis. The hydrolysed dye is no longer reactive and can no longer chemically bond with the fibres. It must be removed from the fabric in subsequent treatments [1].

Polyamides contain an amide functional group (-CO-NH-) in their backbone. The polyamide chain ends on one side with an amino group (-NH₂) and on the other side with a carboxyl group (-COOH). The amino end group is basic and can be protonated to an ammonium ion (-NH₃⁺) under acidic conditions. The carboxyl end group is acidic and can release a proton under basic conditions to form a carboxylate ion (-COO⁻). Reactive dyes can bind

covalently to the amino group of polyamide fibres (-NH₂). Under acidic conditions, the protonation of the amino groups in the polyamide increases the affinity of the anionic dyes to the polyamide. At high pH values, the polyamide is anionic and essentially no fixation occurs due to electrostatic repulsion between the strongly anionic dye and the anionic fibre, although the concentration of -NH₂ groups, the active nucleophilic species that react with the electrophilic groups of the dye, is high. The pH value is one of the key parameters influencing the degree of exhaustion and thus the final fixation of reactive dyes to polyamide [2]. The optimum pH value for good prints has determined to be 4–5 [2–6].

The textile material to be printed must be prepared accordingly before printing, and the dye must be fixed, washed and dried after printing. Absorption and capillary forces in the fibres cause spreading and deteriorate the contour quality. Therefore, the fabric must be impregnated with a thickening agent and suitable fixing agents before printing. The composition of the impregnating bath and the steaming time have a significant impact on the adsorption and fixation of reactive dye on both materials, cotton [7, 8] and polyamide [9].

For printing on cotton, low-viscosity alginate thickeners in low concentrations are used, in which auxiliaries, oxidizing agents and alkalis are dissolved [10, 11]. Various pretreatments have been investigated for polyamide: impregnation with hydroxypropyl methylcellulose [10], impregnation with sodium alginate with alpha-olefin sulfonate [12], O₂ plasma treatment [13] and non-thermal plasma in combination with sublimation printing [14]. Several authors suggested low-viscosity polygalactomannan ethers as thickening agents for polyamide printing [3, 6, 15].

After printing and drying, the dyes are fixed on

the textile. During fixation, the dyes diffuse from the thickening film into the interior of the fibre and bind there. The most common fixation process is one-step normal steaming at 100–103 °C.

Fixation is followed by post-treatments that give the prints their final appearance and improve wet fastness, handle and rub fastness. Non-fixed dyes, thickeners and chemical additives must be removed. Generally, the prints are first washed with cold water and then with hotter wash baths, sometimes with the addition of dispersion soap [1].

The aim of this study was to investigate whether polyamide and blends thereof can be successfully printed digitally with reactive dyes, and which preparation is best suited for this purpose. Four

basic colours were printed on fabrics made of cotton, polyamide and a blend of cotton and polyamide. The CIE $L^*a^*b^*$ colour values, the colour depth (K/S) and the dye penetration (P) were compared on different materials printed under the same conditions. The colour fastness of the prints to rubbing (crock test), light and washing was measured.

2 Experimental

2.1 Materials

Knitted fabrics from the manufacturer Inplet Pletiva d.o.o., Slovenia, were used. Fabric data are presented in Table 1.

Table 1: Knitted fabric data

Material	Label	Horizontal density (stiches/cm)	Vertical density (course/cm)	Mass per unit area (g/m ²)
100% cotton	CO	18	24	149.1
50% cotton/50% polyamide	CO/PA	15	17	217.6
100% polyamide	PA	13	18	100.8

2.2 Preparation of textiles for printing

The fabrics were pretreated with an alginate thickening preparation (A) or a galactomannan thickening preparation (GM). The recipes are presented in Tables 2 and 3.

The following chemicals were used: CHT alginate EHV (Bezema, Switzerland), alginate thickener; Prisulon DCA 130 (Bezema, Switzerland), polygalactomannan ether; sodium hydrogen carbonate (NaHCO_3) (Kemika, Zagreb, Croatia); urea ($\text{CO}(\text{NH}_2)_2$) (J.T. Baker, Netherlands), hydrotropic agent, Rapidoprint XR (Bezema, Switzerland), sodium m-nitrobenzenesulfonate, oxidising agent; and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (Kemika, Zagreb, Croatia).

The fabrics were impregnated using a laboratory two-roller padder (Mathis, Switzerland) with an impregnation effect of 88%. The alginate thickening preparation was applied to cotton and cotton-polyamide blended fabrics. The galactomannan thickening preparation was applied to polyamide and

cotton-polyamide blended fabrics. The impregnated samples were air dried at room temperature.

Table 2: Recipe for the preparation of the alginate thickener

Additive	Amount (g)
CHT-alginat EHV 4%	400
Distilled H_2O	525
NaHCO_3	15
$\text{CO}(\text{NH}_2)_2$	50
Rapidoprint XR	10
Total	1000

Table 3: Recipe for the preparation of galactomannan thickener

Additive	Amount (g)
Prisulon DCA 130. 8%	910
Citric Acid 0.2%	90
Total	1000

2.3 Printing, fixation and after-treatment

Printing was performed using a digital piezo DOD printer TextileJet Tx2-1600 from Mimaki with a resolution of 720 dpi and reactive dyes Jettex R (DyStar, England). The patterns were pre-processed as squares in Adobe Photoshop. 100% cyan, 100% yellow, 100% magenta and 100% black were printed.

The printed fabrics were fixed in a laboratory steamer DHE 20675 (Werner Mathis AG, Switzerland) in 90% saturated steam at 102 °C. Cotton was steamed for 10 minutes and polyamide for 20 minutes, while the blends were steamed depending on the preparation: 10 minutes for the alginate preparation and 20 minutes for the galactomannan preparation.

After fixation, the fabric was first rinsed with cold water to remove residual thickeners, chemicals and some unfixed dyes, then with warm water and finally with hot water. The next step was soaping for five minutes at 100 °C with 1 g/l CIBAPON R detergent (CIBA, Switzerland) to remove all remaining dye residues. After soaping, the samples were rinsed with warm and cold water and air-dried at room temperature.

2.4 Analyses

The colour coordinates CIE $L^*a^*b^*$ and the reflectance R (%) of the printed samples were measured using a SF 600 PLUS-CT spectrophotometer (Datacolor International, Switzerland). Ten measurements were taken for each colour on each print. The measurements were taken on the front and back of the printed fabric. The measurement conditions were: standard light D65, standard observer 10°, device geometry d/8°, measuring range 400–700 nm, four fabric layers and a measuring aperture of 20 mm.

The colour difference (ΔE^*) was calculated from the CIE colour coordinates $L^*a^*b^*$ according to equation 1 [16]:

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where ΔL^* represents the difference in lightness, Δa^* represents the difference on the red-green axis

and Δb^* represents the difference on the yellow-blue axis.

The colour depth values (K/S) of the prints were calculated from the reflectance measurements using equation 2 [16]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (2)$$

where K represents the absorption coefficient (depending on the dye concentration), S represents the scattering coefficient and R represents the reflectance of the sample at a specific wavelength ($R = 0 - 1$).

The penetration coefficient, P , indicates the amount of dye that has reached the back of the fabric. It was calculated according to equation 3 [1]:

$$P = \frac{\frac{K/S(back)}{(0.5 \times [K/S(front) + K/S(back)])}}{\times 100 (\%)} \quad (3)$$

where $K/S(front)$ represents the colour depth on the front side of the sample and $K/S(back)$ represents the colour depth on the back side of the sample.

Rub fastness was determined according to the standard SIST EN ISO 105-X12:2002 – Colour fastness to rubbing. Rubbing was carried out using a Crockmeter (Electronic Crockmeter; SDL Atlas, USA).

Light fastness was determined according to the standard SIST EN ISO 105-B02:2014 – Colour fastness to artificial light: Xenon arc lamp test on a Xenotest Alpha (Atlas, USA).

Colour fastness to washing was determined according to the standard ISO 105-C01:1989 – Textiles – Colour fastness tests – Part C01: Colour fastness to washing: Test 1. Depending on the raw material composition of the sample, one accompanying fabric was made of cotton and another of polyamide. The 10 x 4 cm samples were washed with the accompanying fabrics in a Launder-ometer LDH-HT B-S (Atlas Electric Devices, USA).

3 Results and discussion

Table 4 presents the results of the CIE $L^*a^*b^*$ colour values of CMYK prints on cotton, polyamide and cotton-polyamide blended fabrics impregnated with different preparations. For all colours except magenta, the CIE L^* value is lowest on cotton, indicating

that prints on cotton are darker than on polyamide and cotton-polyamide blended fabrics, regardless of the preparation used. The calculated colour differences, ΔE^* , show that the colours printed on various materials differ significantly. The differences are smallest for magenta, but even here they are greater than 1 and therefore visible to the naked eye.

Table 4: CIE $L^*a^*b^*$ values on cotton (CO), polyamide (PA) and blended fabrics (CO/PA) impregnated with alginate (A) or galactomannan (GM) as thickener, and colour differences (ΔE^*) between prints on CO and other materials

Colour	Material	L^*	a^*	b^*	ΔE^*
C	CO	53.14	-30.31	-28.11	-
	CO/PA (A)	69.10	-11.41	-26.97	24.76
	PA	69.61	-13.56	-26.64	23.54
	CO/PA (GM)	75.05	-10.68	-24.82	29.60
M	CO	53.37	54.58	-3.05	-
	CO/PA (A)	53.49	58.73	-10.66	8.67
	PA	51.63	58.55	-6.92	5.81
	CO/PA (GM)	57.22	56.23	-11.99	9.87
Y	CO	79.07	5.77	87.53	-
	CO/PA (A)	86.52	-1.26	43.65	45.06
	PA	85.93	-3.78	75.52	16.81
	CO/PA (GM)	87.89	-8.25	70.19	23.98
K	CO	18.95	-2.14	-0.01	-
	CO/PA (A)	45.88	16.80	-1.63	32.96
	PA	33.02	23.25	4.56	29.39
	CO/PA (GM)	33.60	24.78	6.24	31.28

Figure 1 shows the spectra of the K/S values as a function of the wavelength (360 nm to 700 nm). The colour depth (K/S) is highest for cyan, yellow and black on CO, which again indicates that prints on CO are darker than prints on PA and blends, regardless of the preparation used. The K/S values are similar for all fabrics for magenta.

CO/PA blends have lower K/S values than CO and PA, regardless of the preparation used. The differences in the K/S values between the blends are small, so that the current measurements cannot confirm the superiority of one preparation over another. From this it can be deduced that the dye binds to CO and not to PA in the alkaline preparation

with alginate thickener. Conversely, the dye binds to PA and not to CO in the acidic preparation with galactomannan thickener. The blends are therefore printed in lighter shades.

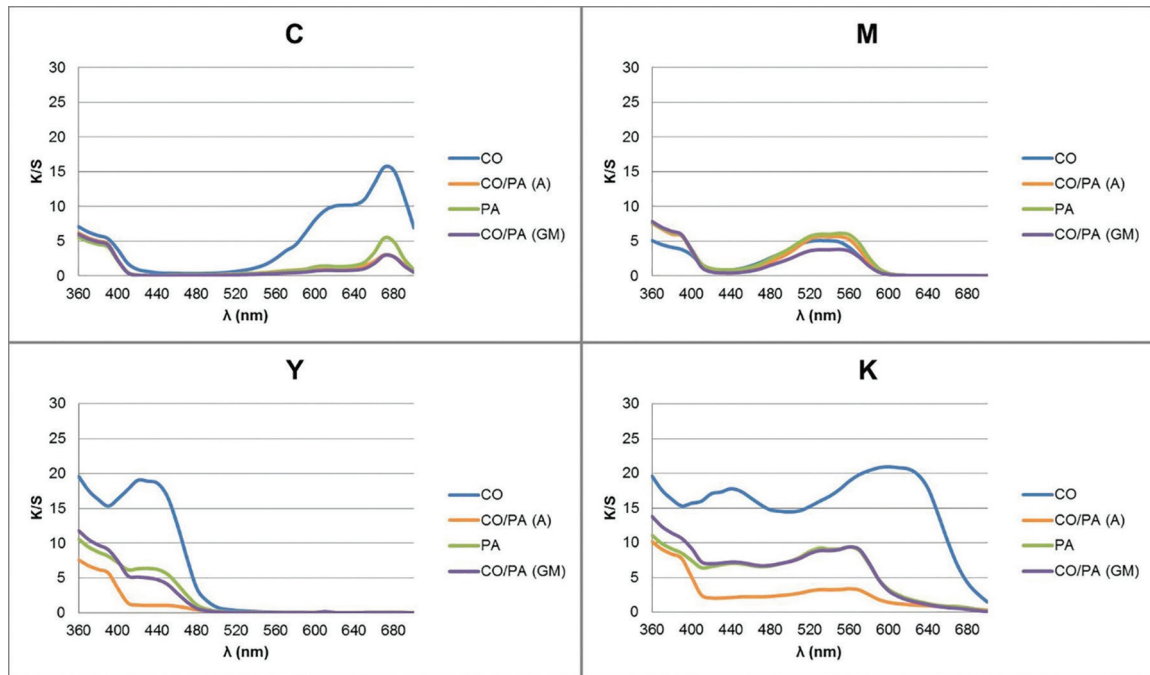


Figure 1: K/S values of CMYK prints on cotton (CO), polyamide (PA) and blended fabrics (CO/PA) impregnated with alginate (A) or galactomannan (GM) as a thickening agent

Figure 2 shows the degree of penetration of the CMYK colours. The lowest penetration can be seen with CO. PA has a higher penetration than CO, which means that the dye solution migrates more to the back of the fabric. This can be explained by the fact that polyamide fibres are hydrophobic and absorb much less water than cellulose fibres, which leads to slower dye diffusion into the fibres and more difficult access to the available amino groups.

The highest penetration is observed with blends, especially with CO/PA(A). The high penetration is one reason for the low K/S values on the front side of the fabric. Dye that is transferred to the back of the fabric and binds there is less visible, resulting in a lower colour depth. Comparing the effects of preparation, the prints on CO/PA (A) generally have higher penetration than on CO/PA (GM).

Table 5 presents the colour fastness values of the prints for dry and wet rubbing according to the grey scale. The results show that all prints have good fastness to dry rubbing, with very high values of 4–5.

The values for wet rubbing vary. The highest wet rubbing fastness is achieved for PA (grade 4) with

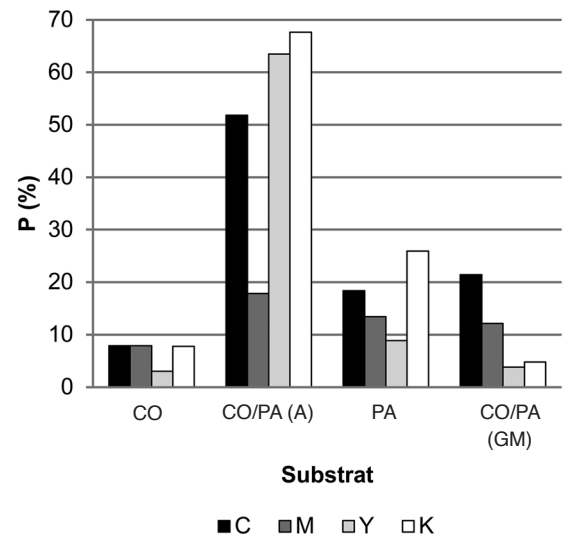


Figure 2: Penetration degree (P) of CMYK prints on cotton (CO), polyamide (PA) and blended fabrics impregnated with alginate (CO/PA(A)) or galactomannan (CO/PA(GM)) as a thickening agent

cyan, magenta and black, and for the blend CO/PA (GM) with magenta and black. The values are lower for CO and CO/PA (A), with the lowest rub fastness being achieved for CO with cyan (score 1), and for

the CO/PA (A) blend with cyan, yellow and black. This can be explained by the fact that the absorption of the dyes by the cotton is higher than their fixation. Cotton also absorbs hydrolysed dye, which cannot react with the fibres. Hydrolysed dye that was not removed in final rinsing steps becomes visible during wet rubbing. PA, as a less absorbent material, absorbs less hydrolysed dye, and this can also be removed more easily during rinsing. The wet rubbing results are therefore better for PA.

As the highest wet rubbing fastness applies to PA, this is also the case with the CO/PA (GM) blend, as the dyes in this case are predominantly bound to PA and not to CO.

Table 5: Colour fastness values to rubbing on cotton (CO), polyamide (PA) and blended fabrics (CO/PA) impregnated with alginate (A) or galactomannan (GM) as thickening agents

Colour	Material	Dry rubbing	Wet rubbing
C	CO	4	1
	CO/PA (A)	4	1
	PA	5	4
	CO/PA (GM)	5	3
M	CO	5	2
	CO/PA (A)	5	2
	PA	5	4
	CO/PA (GM)	4	4
Y	CO	5	2
	CO/PA (A)	4	1
	PA	4	3
	CO/PA (GM)	4	3
K	CO	4	3
	CO/PA (A)	5	1
	PA	4	4
	CO/PA (GM)	4	4

Table 6 presents the colour fastness values of the samples to light. From this it can be concluded that light fastness depends primarily on the dye and less on the fabric on which they are printed. Regardless of the fabric, the highest light fastness is for yellow, lower for magenta and black, and the lowest for

cyan. Within the individual dyes, the values are better for CO and PA, and worse for blends, regardless of the preparation used. The reason for this is that less dye is bound in blends, so that the dyes are more accessible to light and the discoloration is therefore more visible. The highest rating is 7 for yellow on PA, while the lowest is 1 for cyan on the blend CO/PA (GM).

Table 6: Light fastness values of samples on cotton (CO), polyamide (PA) and blended fabrics (CO/PA) impregnated with alginate (A) or galactomannan (GM) as thickening agent

Colour	Material	Light fastness
C	CO	5
	CO/PA (A)	2
	PA	2
	CO/PA (GM)	1
M	CO	2
	CO/PA (A)	3
	PA	4
	CO/PA (GM)	3
Y	CO	6
	CO/PA (A)	3
	PA	7
	CO/PA (GM)	4
K	CO	4
	CO/PA (A)	2
	PA	3
	CO/PA (GM)	2

Table 7 shows the colour fastness values of the prints when washed at 40 °C. The 100% CO and 100% PA fabrics recorded the best values for colour change, although they are not excellent, which means that some of the dye (hydrolysed dye) is removed during washing. The values are lower for blended fabrics. The reason for this is the same as for light fastness. Less dye is bound on blended fabrics than on CO and PA fabrics, so the reduction in the amount of dye on the fibres due to washing is more visible.

The ratings for dye transfer to cotton and polyamide adjacent fabric are similar for all dyes and

fabrics. The ratings range from 3 to 4–5. Staining on the adjacent fabrics is relatively low, indicating that the washed-out dye does not stain the adjacent fabrics.

Table 7: Wash fastness values at 40 °C of cotton (CO), polyamide (PA) and blended fabrics (CO/PA) impregnated with alginate (A) or galactomannan (GM) as a thickening agent

Colour	Material	Washing fastness		
		Colour change	Staining of CO	Staining of PA
C	CO	4–5	4	4–5
	CO/PA (A)	2	3–4	4
	PA	4	3–4	4
	CO/PA (GM)	3	4	4
M	CO	3–4	4–5	3–4
	CO/PA (A)	3	4	3
	PA	4	3–4	4
	CO/PA (GM)	2	4	4
Y	CO	3–4	4–5	4
	CO/PA (A)	2	4	3–4
	PA	4	3–4	4–5
	CO/PA (GM)	2–3	4	3–4
K	CO	4	4	4
	CO/PA (A)	2–3	3–4	4
	PA	4–5	3	4
	CO/PA (GM)	4–5	4	3

4 Conclusion

The colour depth of prints is highest on cotton, lowest on polyamide and even lower on blended fabrics for all colours. The lightness values (CIE L*) are consequently lowest for cotton, slightly higher for polyamide and highest for blended fabrics. Visually, the colours appear intense and bright on cotton and polyamide, while they are significantly lighter and less intense on blended fabrics.

Reactive dyes adhere well to cotton with the alkaline alginate preparation (pH 9) and to polyamide with the acidic galactomannan preparation (pH 5.5). Good colour values were achieved in both cases. In blends, the colours are lighter and the colour values lower because the pH value of the preparation is only suitable for one component in the blend. In the alkaline alginate preparation, the reactive dye binds well to cotton but poorly to polyamide. In the acidic

galactomannan preparation, the dye binds well to polyamide but poorly to cotton. This means that one component of the blend is dyed poorly or not at all.

The degree of dye penetration also influences the K/S values. If the dye is transferred to the back side of the fabric, it is not visible on the front side. In our cases, polyamide is more hydrophobic and therefore absorbs less dye than cotton, so more dye is transferred to the back and penetration is high. In blends, one component is polyamide, which transfers the dye to the back, while the other component does not bind the dye due to the unsuitable pH value. The penetration is therefore even higher. The highest percentage of dye on the back of the fabric, is found for all colours on the cotton/polyamide blend impregnated with alginate thickener, and the lowest on the 100% cotton fabric.

All prints exhibit good fastness to dry rubbing, while the fastness values to wet rubbing are moderate. The best fastnesses to wet rubbing value were

recorded on polyamide and the cotton-polyamide blend impregnated with galactomannan thickener, as these fabrics absorb less hydrolysed dye. Light fastness is best for 100% cotton and 100% polyamide and worse for blends, regardless of the preparation used. Wash fastness is good for 100% cotton and 100% polyamide and worse for blends, regardless of the preparation used.

In summary, polyamide fabrics impregnated with acidic galactomannan thickener can be successfully printed digitally with reactive dyes, although the colour tones achieved are slightly lower than those obtained with cotton fabrics impregnated with alkaline alginate thickener. The light fastness, wash fastness and fastness to rubbing are acceptable. Cotton/polyamide blends can also be digitally printed with reactive dyes, although the colour tones are even lower than those of polyamide and cotton and the fastness properties are poorer. The superiority of the alkaline alginate preparation or the acidic galactomannan preparation cannot be confirmed on the basis of the current measurements. The results are similar for both. Lower K/S values are related to less favourable pH conditions for the binding of the dye to one component of the blend and a high penetration of the dye to the back of the fabric.

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