ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PIGMENT PRINTING OF COTTON FABRICS WITH CYCLODEXTRIN AND BIFUNCTIONAL REACTIVE DYE

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Abstract: *Beta-cyclodextrin, which has seven glucopyranose units, have ability to make inclusion complexes with the appropriate molecules that are called guest molecules. The inclusion complex occurs in the apolar cavity of beta-cyclodextrin therefore guest molecules should have the appropriate apolar groups and molecular size. Cyclodextrins can change the some properties of guest molecules, such as solubility, thermal behavior etc. Beta-cyclodextrin, has been preferred to use in various textile applications, such as insecticide, cosmetics, pharmaceutical agents, antibacterial agents, odour applications, and in dyeing as an auxiliary agent. However, a few studies are done using cyclodextrins in printing. Printing of pigment dyes with reactive printing paste using beta-cyclodextrin was investigated in this work. By this purpose, in the first step inclusion complexes were obtained by kneading method at various weight ratios of beta-cyclodextrin and pigments. Inclusion complexes were printed on cotton fabric by flat screen printing with using alginate based reactive printing paste. In the second step, pigments were printed by pigment printing paste with and without of cyclodextrin Reactive dye also was printed with and without cyclodextrin. Colorimetric values, colour strength fastness properties and stiffness peculiarities were investigated. The optimum complex forming weight ratio was found 1:2 for red, blue and mixture of pigments, and 1:3 for yellow pigment from colorimetric and colour strength values. Crocking fastness were improved by addition of inclusion complexes.*

Key words: *Fastness, Printing, Inclusion complex, Colour strength, CIEL*a*b**

1. INTRODUCTION

Beta-cyclodextrin, which has seven glucopyranose units, has been preferred to use in various textile applications [1]. Many investigations were performed for dyeing process due to its capability to form inclusion complexes with common textile dyes. Especially cyclodextrins are studied as additive in dyeing of cotton [2], [3]. and emulsifier in washing process [3], [4]. Unfortunately, a few studies are performed in printing of textiles. Knittel, Buschmann & Schollmeyer (1996), investigate the usage of derivatives cyclodextrin to be alternative to urea. They investigate the viscosity of printing paste and dye fixation and found that monochlortriazinyl derivative of beta-cyclodextrin improves the dye fixation [5]. The effect of monochlortriazinyl derivative of beta-cyclodextrin on rheological behaviours, colour strength and fastness properties is investigated [6]. Monochlortriazinyl derivative of beta-cyclodextrin is used in printing of wool/polyester fabrics. First the fabrics are modified by cyclodextrin derivative and then are printed by paste of disperse dye [7].

As well known reactive dyes have reactive groups, which reacts with hydroxyl groups of cellulose macromolecules. The reactive dyeing or printing are performed at basic conditions, however besides reaction between hydroxyl of cellulose and reactive group, reactive groups can react with hydroxyl groups of water molecules. Bifunctional reactive dyes have been introduced owing to avoid of reaction between water and reactive groups. Bifunctional reactive dye was used as a bridge between cyclodextrin and cellulose [8].

Printing of pigment dyes with reactive printing paste was investigated in this work. By this purpose, in the first step inclusion complexes were obtained by kneading method at various weight ratios of beta-cyclodextrin and pigments. Inclusion complexes were printed on cotton fabric by flat screen printing with using alginate based reactive printing paste. In the second step, pigments were printed by pigment printing paste with and without of cyclodextrin Reactive dye also was printed with and without cyclodextrin. Colorimetric values, colour strength fastness properties and stiffness peculiarities were investigated.

2. EXPERIMENTAL

2.1 Materials

Commercial beta-cyclodextrin Periplex CDP (β-CD) was supplied by Dr. Petry Textile Auxiliaries (Turkey). Three pigment dyes (Lyosperse Yellow M3G liq-CI Pigment Yellow 17, Lyosperse Red 2BN liq-CI Pigment Red 146, Lyosperse Blue G liq-CI Pigment Blue15:3) and a bifunctional reactive dye (Novacron Orange PH-3R-CI Reaktive Orange 131) (Huntsmann) were used. Alginate based Lyoprint RD-HT (Huntsman) for reactive printing and polyacrilic acid derivative (PTF) for pigment printing were used as thickener. (Table 1) All chemicals were commercial grade and used without any purification. Methanol (merck) and purified water were used for kneading process of inclusion complexes. All printing process achieved by using soft water.

2.2 Methods

Kneading process was performed according to Taneri et al. (2003) [9]. Kneaded products were prepared in three pigments: β-CD weight ratios (1:1, 1:2 and 1:3). After preparation of complexes, they introduced into reactive printing paste. Reactive dye also was printed alone and with addition of β-CD in 1:1 weight ratio. Fixation of printed goods was achieved by steaming at 102 ^{o}C for 10 minutes. Washing-off procedures are in order of 2 cold rinses, 2 hot wash at 90 ^{o}C for 10 minutes with 1 g/l Eriopon R (Huntsman) dispersant, warm rinse, cold rinse, neutralize to pH 7 and finally a cold rinse.

Table 1. *Printing pastes reciepes*

Reactive Printing Paste Recipe			**Pigment Printing Paste Recipe**	
Ingredient	Amount (g)		Ingredient	Amount
Lyoprint RD-HT	25		Ammonia (ml)	20
Urea	100		PTF (g)	30
Chelating agent	4	Paste A	Binder (g)	60
Sodium carbonate	4		Water (g)	X
Sodium bicarbonate	28		Total (g)	1000
Calgon T	4		Emulsifier (ml)	10
Ludigol	12	Paste B	White Sprit (g)	150
Water	X		Urea (g)	20
Total	1000		Paste A (g)	Y
			Total (g)	1000

Printing paste of pigment dyes was prepared according to recipes for reactive and pigment printing, which were given in Table 1. Pigment dyes were printed alone and with addition of β-CD in 1:1 weight ratio. Fixation of printed goods was achieved by thermofixation at 140 ^{o}C for 4 minutes. After printing a cold washing-off procedure was employed.

Colorimetric values (CIE L*a*b*C*H) of printed fabrics were measured by Minolta 3600D spectrophotometer (D65, specular included, 10^{o}). To determine the colour strength, K/S values at the wavelength of maximum absorption were calculated from the formula (Kubelka-Munk) by using spectrophotometer (Minolta -3600D). Washing fastness tests were carried out according to ISO 105-.C06 method of A1S. Crocking fastness was measured according to ISO 105-X12. Stiffness of printed fabrics was determined according to TS 1409 by using flexometer.

3. RESULTS and DISCUSSION

3.1. CIE L*a*b*C*H values

Colorimetric values of printed fabrics are shown in Table 2. Highest L* (lightness) value was obtained in the case of 1:3 weight ratio, when blue pigment was examined. Chroma, a* and b* values were increased with increasing of weight ratio. Thus the printings of 1:3 pigment: cyclodextrin weight ratio was more vivid and had red and yellow shades. However this fact can be due to using reactive dye as a bridge between the cyclodextrin and cellulose. In the case of yellow pigment, there were no differences between weight ratios of cyclodextrins. This fact can be attributed to yellow shades of both pigment and reactive dyestuff. Lightness and b* values of red pigment was increased with weight ratio. Increasing of yellowness can denote the existence of complex between reactive dyestuff and cyclodextrin. 1:2 weight ratio of red pigment gave highest red values at greenness-redness axis of colour space. Trichromic mixture of pigments, reactive dye and cyclodextrin were also printed to cotton fabrics. Lightness values of mixture printings were not significantly different, however vividness of fabrics were changed. The highest chroma value was observed at 1:2 weight ratio. Dullest shade was observed at 1:3 weight ratio. Hue that is more reddish was observed in the case of 1:2 weight ratio. It can be said that the colorimetric values of mixture printings were dominated by red pigment.

To understand the effect of cyclodextrin on reactive dyestuff, printing of reactive dyestuff and 1:1 cyclodextrin: reactive dyestuff mixture was also applied. All colorimetric values, except lightness value, increased with cyclodextrin addition. Of course cyclodextrin is not only forming complexes with pigments. Also, it can make complexes with non-polar groups of suitable substances. Thereby cyclodextrin can form complexes with both hydrolyzed and non-hydrolyzed reactive dyestuff. Cyclodextrin increased the Yellowness of fabrics increased because of fixation of more reactive dyestuff. Also more reddish and vivid hues were observed with the addition of cyclodextrin.

Printing with printing paste was also investigated. Lightness value of yellow pigment decreased with addition of cyclodextrin. Contrary lightness values of other pigments increased with cyclodextrin. Yellowness of yellow pigment increased with cyclodextrin due to complex between pigment and cyclodextrin. In the case of red pigment, a* values slightly increased with addition of cyclodextrin.

3.2. Colour Strength

Colour strength of printings was observed by K/S values. The highest K/S values were observed at 1:2 weight ratio for red, blue and mixture printings. For the yellow pigment, the highest K/S value was observed at 1:3 weight ratio. Colour strength values were compatible with colorimetric values. Thereby it can be concluded that the optimum complex forming weight ratio

was 1:2 for red, blue and mixture of pigments, and 1:3 for yellow pigment. Addition of cyclodextrin increased colour strength of reactive dye. It can be inferred that cyclodextrin may form complex with both hydrolyzed and non-hydrolyzed reactive dyestuff. Thus colour strength of cyclodextrin added printings were higher than the absence of cyclodextrin. K/S values decreased with cyclodextrin addition in the case of pigment printing.

3.3. Fastness Properties

Fastness properties of printed fabrics depicts in Table 3. In spite of good bleeding properties, colour change values were very poor at reactive printings of pigments, except yellow pigment. Good colour change values of yellow pigment were observed due to colour of reactive dyestuff. Very low bleeding properties obtained for pigment printing paste with cyclodextrin.

Table 2. *Colourimetric and K/S Values*

Printing Paste	Colour	Dye:β-CD Ratio	L*	a*	b*	C*	H	K/S
Reactive Printing Paste	Blue	1:1	53.074	3.486	27.580	27.799	82.791	53.108
		1:2	53.763	2.983	27.949	28.108	83.909	51.857
		1:3	57.219	11.529	37.358	39.097	82.849	57.576
	Yellow	1:1	69.572	33.045	55.542	64.629	59.249	52.285
		1:2	68.066	34.762	56.269	66.141	58.293	57.189
		1:3	68.825	34.116	55.395	65.158	58.373	53.448
	Red	1:1	60.422	40.939	45.218	60.997	47.843	60.288
		1:2	62.045	41.357	47.804	63.211	49.136	60.843
		1:3	64.449	36.966	50.831	62.851	53.974	58.548
	Trichromatic	1:1	63.570	24.519	44.407	50.727	61.095	49.317
		1:2	63.154	25.43	45.927	52.497	61.027	53.527
		1:3	63.743	21.968	41.136	46.634	61.896	45.043
	Reactive	-	72.617	28.212	42.413	50.939	56.369	29.209
		1:1	69.020	34.400	56.766	66.376	58.785	56.400
Pigment Printing Paste	Blue	-	37.699	10.966	38.739	40.261	254.195	15.812
		1:1	42.986	13.640	38.350	40.704	250.422	11.078
	Yellow	-	87.072	2.226	96.640	96.665	1.320	13.023
		1:1	86.190	0.938	98.262	98.266	0.547	12.667
	Red	-	40.939	59.116	22.368	63.206	20.725	14.922
		1:1	45.872	59.991	18.511	62.782	17.149	11.166

Colour fastness to crocking is the characteristic property of pigment printing. If the Table 3 examine, pigment printing pastes had very poor wet crocking fastness. Approximately 1 point increase was observed for kneading method to complex formation and their printing with reactive dyestuff. Highest wet crocking fastnesses were obtained at mixture of pigments as well as reactive dyes. Moderate dry crocking fastnesses were obtained for pigments. Good dry crocking fastnesses were observed for reactive dyestuffs, which were expected.

***Table 3**. Fastness Properties*

Printing Paste	Colour	Dye:β-CD Ratio	Colour change	Washing Bleeding						Crocking	
				Wo	PAC	PES	PA	Co	CA	Wet	Dry
Reactive Printing Paste	Blue	1:1	1	4-5	5	4-5	4-5	5	5	2-3	3
		1:2	1	4-5	4	4	4	4-5	5	2-3	3-4
		1:3	1	5	5	5	4-5	4-5	5	3-4	4
	Yellow	1:1	2-3	4-5	4-5	4-5	5	5	5	2-3	4
		1:2	4	4-5	4-5	5	4-5	4-5	5	3	3-4
		1:3	4-5	5	5	5	5	5	5	3	3-4
	Red	1:1	2	4-5	5	5	4-5	5	5	2-3	3-4
		1:2	2-3	4-5	4-5	4-5	4-5	4-5	4-5	2-3	3-4
		1:3	2-3	4-5	4-5	4-5	4-5	4-5	4-5	3-4	4
	Trichromatic	1:1	4	4	4	4-5	4	4-5	3-4	3-4	4-5
		1:2	2	4-5	4-5	4-5	4	4	4-5	4	4-5
		1:3	3	5	5	4-5	4-5	5	5	4-5	4-5
	Reactive	-	2-3	4-5	4-5	4	4	4-5	4-5	4-5	4-5
		1:1	3	5	5	5	4-5	4-5	5	4-5	4-5
Pigment Printing Paste	Blue	-	4	4-5	4-5	3-4	4	4-5	4-5	2	3-4
		1:1	3	2	2	2	2-3	2	2-3	2-3	3-4
	Yellow	-	4-5	4-5	4-5	4-5	4-5	4-5	4-5	2	3-4
		1:1	3-4	1-2	1-2	2	2	1-2	1-2	1-2	3-4
	Red	-	4	4	4	4	4-5	4	4-5	2	3-4
		1:1	3	1-2	1-2	1-2	2	1-2	1-2	1-2	3-4

3.4. Bending Properties

Fig. 1 shows bending properties of inclusion complexes with reactive printing paste. Bending values were varying between 17.2 and 13.3. Fig. 2 depicts effect of cyclodextrin addition on bending properties of both pigment and reactive printing pastes. Bending properties were enhanced by addition of cyclodextrin in the case of pigment printing paste. However cyclodextrin did not change the handle properties of reactive printing.

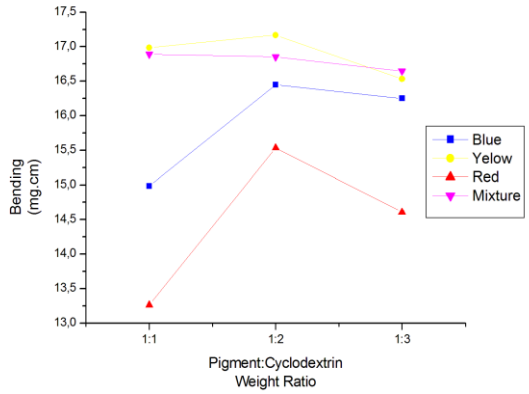

Fig. 1. *Bending Properties of Reactive Printing Paste*

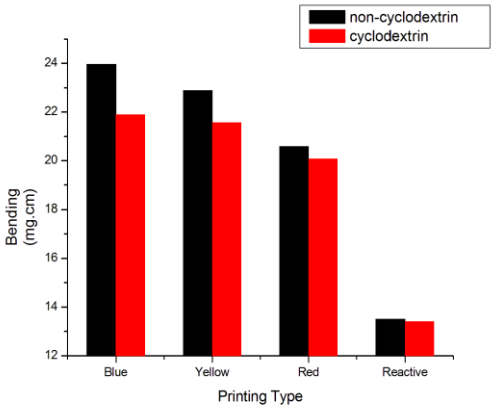

Fig. 2. *Bending Properties of Pigment Printing Paste*

5. CONCLUSIONS

It can be concluded that the optimum complex forming weight ratio was 1:2 for red, blue and mixture of pigments, and 1:3 for yellow pigment from colorimetric and colour strength values. Colour fastness to wet crocking and water spotting values were improved by inclusion complexes. Bending properties were enhanced by addition of cyclodextrin. By looking all the data it can be said that cyclodextrins can be used with bifunctional reactive dyestuff at printing of pigments.

REFERENCES

[1] J. Szejtli, *"Cyclodextrins in the textile industry,"* Starch/Staerke, vol. 55, pp. 191-196, 2003.

[2] U. Denter, E. Schollmeyer, *"Bestimmung der farbstoff-aufnahme beim trichromen färben von baumwolle,"* Textilveredlung, vol. 29, pp. 288-291, 1994.

[3] A. Cireli, B. Yurdakul, *"Application of cyclodextrin to the textile dyeing and washing processes,"* J. Appl. Polym. Sci., vol. 100, pp. 208-218, 2006.

[4] E. Franco, M. Ferrándiz, L. M. Pérez, S. Moldovan, E. Nuñez, J. A. Gabaldón, P. Cosma, P. Fini, E. Perez, M. Ferrándiz, *"Cyclodextrins to recover textile dyes in waste water,"* Annals of The University of Oradea Fascicle of Textiles, Leatherwork, vol. XVI, pp. 31-34, 2015.

[5] D. Knittel, H. J. Buschmann, E. Schollmeyer, *"Beiträge zum reaktivdrucksubtitution von harnstoff,"* Textilveredlung, vol. 31, pp. 153-157, 1996.

[6] A. A. Hebeish, A. A.Ragheb, S. H. Nassar, E. E. Allam, J. I. Abd El Thalouth, *"Technological evaluation of reactive cyclodextrin in cotton printing with reactive and natural dyes,"* J. Appl. Polym. Sci., vol. 102, pp. 338–347, 2006.

[7] N. A. Ibrahim, E. M. R. El-Zairy, *"Union disperse printing and UV-protecting of wool/polyester blend using a reactive β-cyclodextrin,"*Carbohyd. Polym., vol. 76, pp. 244–249, 2009.

[8] W. Chao-Xia, C. Shui-Lin, *"Anchoring -cyclodextrin to retain fragrances on cotton by means of heterobifunctional reactive dyes,"* Color. Technol., vol. 120, pp. 14-18, 2004.

[9] F. Taneri, T. Güneri, Z. Aigner, M. Kata, *"Influence of cyclodextrin complexation on the physicochemical and biopharmaceutical properties of ketoconazole,"* J. Incl. Phenom. Macro., vol. 47, pp. 15–23, 2003.