World Applied Sciences Journal 5 (1): 39-41, 2008
ISSN 1818-4952

Aftertreatment of Polyamide 6 Printed with Anionic Dyes to Improve Staining

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Abstract: Staining of unprinted area during the washing process is one of the most troublesome points in polyamide printing with anionic dyes (especially acid dyes). The present study was conducted to eliminate or reduce the dye deposition to the unprinted area of printed polyamide 6 fabrics, during the washing process. It was found that by the use of specially selected cationic surfactant, syntans and weak alkaline conditions during the washing process the staining problem could be prevented.

Key words: Polyamide 6 · Anionic Dyes · Aftertreatment · Staining · Syntan

INTRODUCTION

Amino end groups (AEG) in Polyamide 6 Fibers are the main reason for the substantivity of the anionic dyes towards these Fibers. Moreover, amino end groups increase the possibility of staining with anionic dyes on Polyamide Fibers [1]. This problem is one of the most troublesome points in polyamide printing. In order to prevent the above mentioned drawback, the use of special aftertreatments has been recommended. An early method of reducing this problem was the use of fullbacktan aftertreatments. The fullbacktan aftertreatment comprises the sequential application of tannic acid and tartar emetic (potassium antimony tartrate) for 30 min at 70°C [2]. This process can impair the handle and impart a shade change to aftertreated samples although it is useful to reduce staining [3]. Nowadays syntans has replaced the fullbacktan to improve the wet fastness of anionic dyes on nylon. Syntans have been described as high molecular weight condensation products of aromatic sulphonic acids. They have anionic groups which are considered to be necessary for the attraction of syntan molecules to polyamides [4]. It is considered that negatively charged groups of the syntan are held by protonated amino groups in polyamide fibers. Therefore it is formed a surface layer on fiber that decreases the diffusion of the dye out of the dyed-syntaned fiber during the washing process as well as ion-ion repulsion between anionic syntan and anionic dye molecules during the wet process. But the exact mechanism has not been cleared yet [3]. It is cleared that the subsequent application of a selected cationic agent to the dyed-syntaned samples can enhance the effect of syntan on polyamide [5]. Afterwards some modifications were done on fullbacktan to reduce their problems (such as impairing the handle and etc.). For example the use of a tin sulfate derived product (Gallofix (Omnichem-Ajinomoto)) [6] or enzyme [7] instead of tartar emetic were proposed. Using tannic acid alone was another method of which the effect of the aftertreatment decreased with increasing temperature of washing [8].

The use of syntan/Gallofix is also a suitable and effective method for the after wash process [9].

In this article the application of some cationic surfactants and a special commercial syntan during the washing process on polyamides printed fabrics with selected anionic dyes was studied in order to reduce or eliminate the after wash staining.

MATERIALS AND METHODS

Polyamide 6 fabric of 24f/170dtex per filament was supplied by Shanghai Ronghua Polyester (China). The fabric was prewashed in a bath containing $1gL^{-1}$ Ultravon GPN (an anionic surfactant supplied by Ciba) and $1gL^{-1}$ Tri sodium Phosphate (Merck) at 70°C for 20 minute. The scoured fabric was rinsed with water at 60°C, followed by cold rinse and then dried. The three anionic dyes listed in table 1, Tinegal W, Tinegal PAC and Sapamin OC (cationic surfactants) and Cibatex RN (syntan) which were supplied by Ciba were used in this study.

All color measurements were carried out using an X-rite spectrophotometer interfaced to a PC using D65 illumination, 10°C standard observer.

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Table 1: Anionic dyes used

Commercial Name	C.I. Number
Erionyl Red RS	C.I. Acid Red 114
Lanaset Black B	C.I. Metal Comp. /Rea. Black Mix
Solophenyl Turquoise Blue BRL	C.I. Direct Blue 199

2.2.Printing: The samples were printed with a printing paste consists of 30-40 g/kg dye, 20 g/kg Irgasol NA, 330 g/kg water, 20 g/kg Urea, 500 g/kg Meyprogum NP-8 (Meyhall), 40 g/kg ammonium oxalate 1:2 and 10 g/kg Albegal FFA.

Then, the fabric was dried, at 100 °C, followed by steam fixation, at 102 °C, for 30 min.

2.3.Common after wash (reference samples): Printed fabrics were rinsed with cold and then at 60 °C water. The rinsed fabrics were soaped in a bath containing $2gL^{-1}$ Ultravon GPN at 60 °C for 20 min, followed by cold rinse.

2.4.Aftertreatment: Each printed fabrics were aftertreated with one of the following cationic surfactants: $2gL^{-1}$ Tinegal PAC, $1gL^{-1}$ Tinegal W (plus $1gL^{-1}$ sodium carbonate) and $2gL^{-1}$ Sapamin OC, at 40 °C for 15 min., finally fabrics were rinsed under the tap water and then, were treated in a bath with $3gL^{-1}$ Cibatex RN for 20 min., at 40°C, finally rinsed with $2gL^{-1}$ sodium carbonate and cold water.

RESULTS AND DISCUSSION

The aftertreatments were carried out using three different kinds of cationic surfactants.

Table 2 shows the colorimetric data for printed fabrics washed with common method (reference samples) and unprinted fabrics. As expected, the staining on unprinted areas of the washed fabrics was obvious. It seems that the structure of Ultravon GPN, which is an anionic surfactant, may be the cause of migration of unfixed dyes from the printed areas to the washing bath and result in staining of printed fabrics.

Table 3 reveals the data obtained for aftertreatments with three different cationic surfactants.

It shows the reduction in ΔE values in the cases of red and black shade, but the ΔE value in regarding the blue shade is quite high. So, it seems that the results are related to the structure of the dyes. The suitable results in the cases of red and black samples, can be attributed to the combined use of Tinegal W and sodium carbonate in the after wash bath. The use of these products can reduce the substantivity of dye towards the fabric; and the anion-cation complex between the dyes and Tinegal W could help to reduce staining.

The application of Cibatex RN, with substantivity towards the fiber, by forming a physical layer on the surface of the polyamide, could reduce migration of the

Table 2: Colorimetric data obtained for reference samples and unprinted samples

		L^*	a^*	b^*	C^*	h	ΔE	Staining
Unprinted fabric		91.38	-0.36	4.98	5.00	94.10	—	—
Red fabric	Printed area	36.33	54.74	32.81	63.82	30.94	—	—
	Unprinted area	71.59	32.57	6.44	33.20	11.18	38.44	1-2
Blue fabric	Printed area	47.03	-26.51	-32.70	42.10	230.97	—	—
	Unprinted area	73.77	-19.91	-15.03	24.94	217.05	33.05	1-2
Black fabric	Printed area	15.30	0.52	-1.03	1.16	296.76	—	—
	Unprinted area	75.99	-0.18	-1.26	1.27	262.09	16.60	2-3

ΔE is color difference between unprinted fabric and unprinted area of printed fabric

Table 3: Colorimetric data obtained for printed fabrics treated with Tinegal W and sodium carbonate

	L^*	a^*	b^*	C^*	h	ΔE	Staining
Red	88.84	2.64	5.19	5.82	63.03	3.93	4-5
Black	88.14	0.09	2.50	2.51	87.99	4.10	4-5
Blue	83.92	-10.60	-4.31	11.45	202.13	15.71	2-3

Table 4: Colorimetric data obtained for printed fabrics treated with sodium carbonate

	L^*	a^*	b^*	C^*	h	ΔE	Staining
Red	83.75	13.31	4.38	13.84	18.43	15.50	3
Blue	84.34	-8.61	-2.73	9.03	197.58	13.30	3
Black	77.49	-0.30	-0.10	0.32	197.60	14.78	2-3

Table 5: Colorimetric data obtained for printed fabrics treated with Tinegal PAC and Sapamin OC

	Process	L^*	a^*	b^*	C^*	h	ΔE	Staining
Blue	Tinegal PAC	90.18	-1.50	4.04	4.31	110.33	1.90	4-5
Black		87.95	-0.41	4.68	4.69	95.00	3.44	4
Red		89.28	0.76	5.22	5.28	81.73	2.39	4-5
Blue	Sapamin OC	88.77	-4.46	1.64	4.75	159.83	5.89	4
Black		83.68	-0.49	-0.04	0.49	184.15	9.19	4
Red		85.90	9.12	4.87	10.34	28.09	10.95	3-4

dyes out of the fabrics and also prevent the dye molecules in the washing bath to enter the fibers. Rinsing with sodium carbonate can also reduce the substantivity of dye molecules towards the fibers.

In order to study the effect of the presence of Tinegal W in the washing bath, Tinegal W was omitted from the washing formula and a higher amount of sodium carbonate was used. As it is stated in Table 4, the results are unacceptable. So we can state that the presence of cationic surfactants in the washing bath might cause the formation of the anion-cation complex between the dye and the surfactant molecules thus, prevent staining. Although sodium carbonate can reduce the substantivity of the dyes towards the fibers, but the effectiveness of sodium carbonate is less than Tinegal W in this regard.

In this study the effects and the use of two different types of cationic surfactants in after wash process, namely Tinegal PAC and Sapamin OC, was investigated. The results showed in table 5 reveals that the application of Tinegal PAC in washing process has a better result in comparison with the other type used. Tinegal PAC is a quaternary amine which can form complexes with anionic dye molecules in the washing bath. By the use of this method the best result was obtained as far as the staining on the unprinted area in after washing process. Application of Sapamin OC does not have the same results and this surfactant is not as effective as the Tinegal PAC in this regard. It seems that the difference between their structures can cause these different results (Sapamin OC is a cationic surfactant based on carbon acid amide and Tinegal PAC is a solution of a quaternary ammonium salt in water-isopropanol).

CONCLUSIONS

Polyamide fibers printed with anionic dyes usually will be stained during the washing process. In order to reduce the staining effect, different cationic surfactants were used in the washing baths. The findings of this study indicate that the effectiveness of Tinegal PAC in washing bath was more effective than the others. Also the use of Cibatex RN solution then rinsing with sodium carbonate is suggested afterwards.

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