

Influence of Low-Temperature Plasma on the Ink-Jet-Printed Cotton Fabric

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ABSTRACT: This article studies the effect of low-temperature plasma (LTP) on an ink-jet-printed cotton fabric. Owing to the specific printing and conductivity requirements for ink-jet printing, none of the conventional printing chemicals used for cotton fabric can be directly incorporated into the ink formulation. As a result, the cotton fabric requires pretreatment with the printing chemicals prior to the stage of ink-jet printing. The aim of this article is to study the possibility and effectiveness of applying LTP treatment to enhance the performance of pretreatment paste containing sodium alginate so as to improve the properties of the ink-jet-printed cotton fabric. Scanning electron microscopic pictures show that LTP treatment

may cause cracks on the fiber surface and hence more dyes could approach the fiber surface during the ink-jet printing process, leading to a higher dye uptake subsequently. In addition, not only the dye uptake is increased after the LTP treatment but the color-fastness properties and the definition of the final print marks are also improved. Therefore, LTP pretreatment in couple with the ink-jet printing technique could improve the final printed properties of cotton fabric. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3214–3219, 2007

Key words: low-temperature plasma; ink-jet printing; cotton; fiber; surface

INTRODUCTION

The advantages of ink-jet printing are well known and the process has grown recently. The ink-jet printing offers benefits such as speed, flexibility, creativity, and cleanliness.^{1,2} In conventional textile printing of cotton fabric, the reactive dyes are applied with the alkali and other chemicals in the form of a print paste. However, due to the specific purity and conductivity requirements for ink-jet printing, such as viscosity and colorant type,³ none of the conventional printing chemicals can be directly incorporated into the ink formulation. As a result, cotton fabric needs to be pretreated with the printing chemicals prior to the stage of ink-jet printing. Most of the commercially pretreated cotton fabrics available in the market for ink-jet printing have been padded with pretreatment paste. However, for commercial reasons, the contents of this paste are not disclosed, resulting in very high prices for this type of fabric. In previous researches, the newly developed pretreatment paste prepared by sodium alginate, sodium bicarbonate, and urea could produce a better result than the commercially pretreated cotton fabrics.⁴ The sodium alginate is usually used as a thickener in the pretreatment paste in ink-jet

printing with reactive dyes due to its ready solubility and excellent stability even after high-temperature fixation treatments.⁴ During the ink-jet printing process, the sodium alginate was coated on the cotton fabric surface to facilitate the ink-jet printing. Therefore, the effectiveness of coating sodium alginate on the cotton fabric will affect the final properties of ink-jet-printed cotton fabric. Recently, low-temperature plasma (LTP) treatment has been proved to be an effective pretreatment method for improving coating process.^{5,6} The aim of this article is to study the possibility and effectiveness of applying LTP treatment to enhance the sodium alginate coating so as to improve the final color properties of the ink-jet-printed cotton fabric.

EXPERIMENTAL

Fabric

100% singed, desized, scoured, and bleached cotton fabric with plain weave structure, 40s × 40s, 133 ends/in. × 72 picks/in., and 136 g/m² fabric weight was used for the experiment.

LTP treatment

A glow-discharge generator (Showa, Japan) was used for the LTP treatment of the cotton fabrics. The glow discharge apparatus was a radiofrequency etching system operating at 13.56 MHz and using an

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aluminum chamber with an internal diameter of 200 mm. A nonpolymerizing gas, namely oxygen, with a flow of 20 cc/min was used. The discharge power and system pressure were set at 80 W and 10 Pa, respectively. The duration of LTP treatment was 1, 2, 5, 15, 30, and 60 min. Five specimens were prepared for each duration of treatment. After LTP treatment, the fabrics were conditioned before being used.

Preparation of pretreatment paste

Unless otherwise stated, all chemicals used were of AR grade. A stock sodium alginate was prepared by dissolving 50 g sodium alginate in 950 mL of deionized water. The amount of sodium alginate used in the pretreatment paste was measured directly from the stock sodium alginate. The pretreatment paste was prepared by adding 150 g sodium alginate, 8 g sodium bicarbonate, and 10 g urea together, finally making up to a weight of 200 g with deionized water. Such pretreatment paste could produce a better color yield of printed cotton fabric when compared with the commercially available cotton fabric.^{4,7} After well mixing the pretreatment print paste, the pH of the pretreatment print paste was adjusted and kept at pH 9–10.

Fabric pretreatment

The well-mixed pretreatment paste was padded onto the cotton fabric using a padding machine (T.K.HOMO Mixer, model HV-M) with an even pressure of 2.6 kg/m² and a constant padding speed of 2.5 rpm until a pick-up of 80% was achieved. The pretreated fabrics were dried in an oven at 80°C and then conditioned before ink-jet printing.

Printing procedure

The model of ink-jet printer used was Mimaki Tx2-1600 (Mimaki Engineering, Japan) with a piezo electric drop on demand print head. A commercially available reactive ink of yellow color with vinylsulphone reacting system^{8,9} was used without further purification. A pattern of square with the size of 80 mm × 80 mm was generated by Dua Graphic Systems software and through TexPrint software to commence operation with 360 dpi × 360 dpi for easy comparison. The printed color can represent a spot color printed on the fabric.

Fabric posttreatment

After printing, the fabrics were air-dried and then put into a steamer. All the printed fabrics were treated with superheated steam at 110°C for 5 min for color fixation.^{4,7} The steamed fabric samples were finally washed in 10 g/L nonionic detergent

until all the unreacted dyes and chemicals were removed from the fabric surface.

Color yield measurements

The printed fabrics were conditioned before color yield measurement with a Macbeth Color Eye 7000A Spectrophotometer. The condition for measurement was set under specular excluded with large aperture. The fabric was folded two times for ensuring opacity and measured twice, i.e., measured on both the warp and weft directions to obtain average results.

The color yield expressed as a *K/S* value ranging from the wavelength of 400 to 700 nm with 20 nm interval within the visible spectrum was calculated. The *K/S* values were summed up according to eq. (1). The higher the *K/S* (sum) value, the more the dye-uptake will be, resulting in better color yield.

$$K/S = (1 - R)^2/2R \quad (1)$$

where *K* is absorption coefficient, depending on the concentration of colorant, *S* is scattering coefficient, caused by the dyed substrate, and *R* is reflectance of the colored sample.

Yellowness index

Yellowness index was measured after the LTP treatment and padding with the pretreatment paste. The yellowness index was measured in accordance with the ASTM Designation: E 313-05. Macbeth Color Eye 7000A Spectrophotometer was used to check the yellowness index of the fabrics with 10° observer under *D*₆₅ for interpreting the data.

Scanning electron microscopy

The surface morphology of the fabrics was investigated by a scanning electron microscope (JEOL, model JSM-6335F) with a magnification of 10,000.

Color-fastness tests

The color fastness of the printed fabrics was assessed by the AATCC Test Method 16-2001 (color fastness to light), AATCC Test Method 61-2001 (color fastness to laundering), and AATCC Test Method 8-2001 (color fastness to crocking).

Outline sharpness measurements

To compare the outline sharpness of the prints, the width of the printed pattern in both warp and weft directions was measured using an optical light microscopy (Nikon Optiplot-pol) with a magnification of 400.

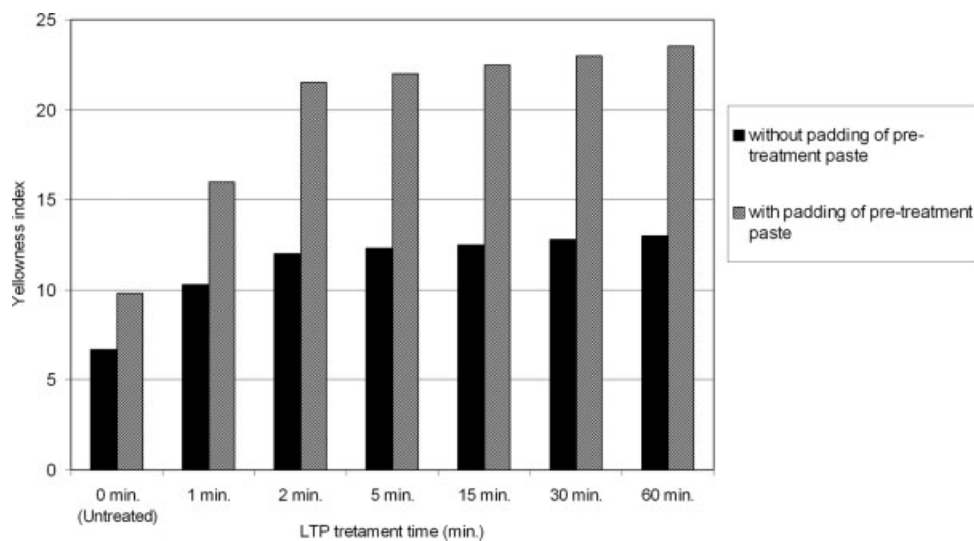


Figure 1. Yellowness index of cotton fabrics with different LTP treatment conditions.

RESULTS AND DISCUSSIONS

Yellowness index

The yellowness indices of the LTP-treated fabric with or without padding of pretreatment paste containing sodium alginate were shown in Figure 1. The measurement of yellowness indices of the LTP-treated fabrics was conducted immediately after the LTP treatment. With regard to the pretreatment paste padded fabrics, the yellowness indices were measured right after the padding and drying process.

Figure 1 shows that when the exposure time of LTP treatment was prolonged, the degree of yellowness increased accordingly. The untreated fabric sample had the lowest yellowness index, whereas the fabric samples treated by LTP treatment for 60 min had the highest yellowness index value. However, the overall changes in yellowness index were not so obvious when the time of LTP treatment was changed from 2 to 60 min.

The main reason of causing yellowness on the fabric samples was probably due to the change of surface properties of fabric samples after subjecting to the LTP treatment. It seemed that the oxygen plasma used in the LTP treatment might cause an oxidation damage on the fabric surface after a certain period of time.^{10,11} The longer the LTP exposure time, the greater the fiber damage would be. As a result, the degree of yellowness was dependent on the LTP treatment conditions such as treatment time and plasma gas. Furthermore, the yellowness might also be due to the high ablation rate caused by the oxygen plasma, leading to the fast removal of yellow component subsequently.¹² As a result of the compromising effect

between the surface oxidation and the removal of yellow component from the fabric surface, the yellowness index of the LTP-treated fabric that had no pretreatment paste did not change significantly during the LTP exposure period between 2 and 60 min.

The relationship between LTP treatment time and degree of yellowness of the fabric samples became more obvious when the fabric had been padded with pretreatment paste as shown in Figure 1. There was an increase in the overall degree of yellowness of the LTP-treated fabric samples padded with pretreatment paste when compared with the LTP-treated fabric samples only. Even the yellowness index of untreated fabric that had no LTP treatment was increased from 6.7 to 9.8 after being padded with pretreatment paste. Those treated by LTP treatment would become much yellower than before after padding with pretreatment paste. Since the drying process should not bring any chemical impact on the fabric samples, thus the occurrence of yellowness on the fabric samples might be due to the combined effect of LTP treatment and sodium alginate present in the pretreatment paste. Hence, it was postulated that sodium alginate in yellow color naturally could contribute certain degree of yellowness to the LTP-treated fabric.

When comparing the data of the yellowness index with those that had no pretreatment paste, it was observed that the pretreatment paste did influence much on the yellowness index of LTP-treated fabric. The yellowness index increased with the prolonged LTP exposure time coupled with the padding of pretreatment paste, but the yellowness index did not change much during the LTP exposure period of 2–60 min.

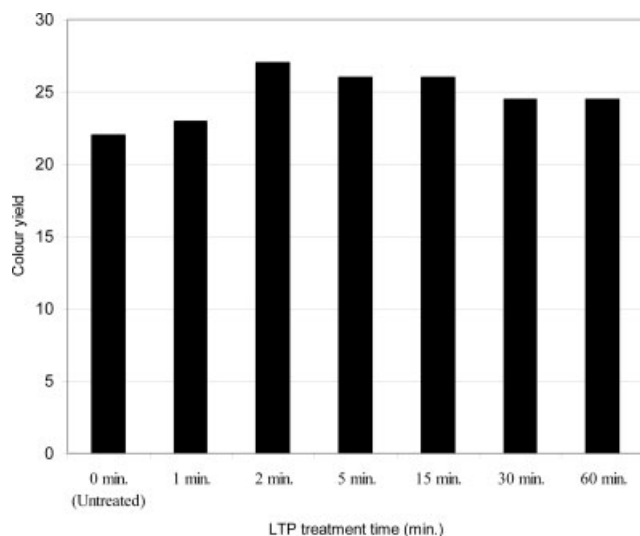


Figure 2 Color yield of the printed fabrics with LTP treatment.

Color yield measurement

Figure 2 shows that the color yield of the LTP-treated fabrics with different treatment time was higher than that of the untreated fabric. The color yield increased gradually with LTP treatment time and reached the maximum at 2 min of treatment time. Further increase of LTP-treatment time did not give further enhancement of the color yield but getting a gradual color yield reduction instead.

Urea is gradually used in print paste as it can swell the cotton fibers during steaming process, especially superheated steaming, so that dye can penetrate into them rapidly.^{12,13} Urea holds some of the water very strongly, and the mixture of urea and water can provide the solvent required for the reaction to occur inside the fibers. Hence, urea acts as a solvent for reactive dye because it performs like a moisture-absorbing agent in the pretreatment paste to increase moisture regain during steaming, thereby accelerating the migration of dye from the thickener film, i.e., the pretreatment paste containing sodium alginate, into the cotton fibers.^{13,14} Since reactive dye with vinylsulphone chemical structure was used in this article, thus it had a tendency to be deactivated in the presence of urea due to the thermal decomposition of urea to biuret and ammonia. This would result in the conversion of the vinylsulphone dye to an inactive aminoethylsulphone rather than a direct reaction between dye and urea, leading to a decrease in the color yield of the LTP-treated fabrics. On the other hand, with a longer exposure time under LTP using oxygen gas, the amount of hydrophilic groups present in the cellulosic fiber such as $-\text{CHO}-$, $-\text{C}=\text{O}$, and $-\text{COOH}$ would increase correspondingly.¹¹ The increased amount of hydrophilic groups

coupled with the urea present in the pretreatment paste could hold more moisture during the steaming process. As a result, hydrolysis of reactive dye might occur and reduce the color yield. In addition, the changes of the hydroxyl groups in the cellulosic fiber into aldehyde and carboxyl groups also decreases the reaction between cellulosic fiber and the reactive dyes and subsequently reduce the color yield.

Scanning electron microscopy

SEM was used for examining the surface changes of the LTP-treated fabric samples as shown in Figures 3–6.

As 2 min of LTP-treatment time gave the maximum color yield in this study, thus the SEM image of LTP-treated cotton fabric with 2-min treatment time was selected for studying, as shown in Figure 4. When compared, it was observed that the untreated cotton fiber surface shown in Figure 3 had a smooth surface, whereas the LTP-treated cotton fiber surface shown in Figure 4 became wrinkled and roughened. The changes in the cotton fiber surface appearance might be due to the localized oxygen plasma ablation of the surface layer causing a surface damage. During the oxygen plasma ablation, the fiber surface was subjected to certain degree of etching. The presence of micropores on the fiber surface indicated this predominant effect of the interaction of oxygen plasma (chemical etching) with the fiber surface. The differential etching of crystalline and amorphous regions might be the origin of the roughness. This process led to an almost complete breakdown of relatively small number of molecules on the fiber surface into very low molecular components, which would eventually vaporize in the low-pressure

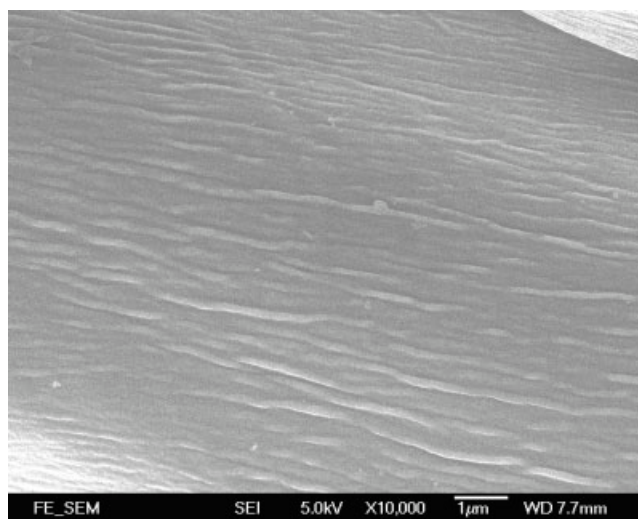


Figure 3 Untreated fabric without pretreatment paste coating ($\times 10,000$).

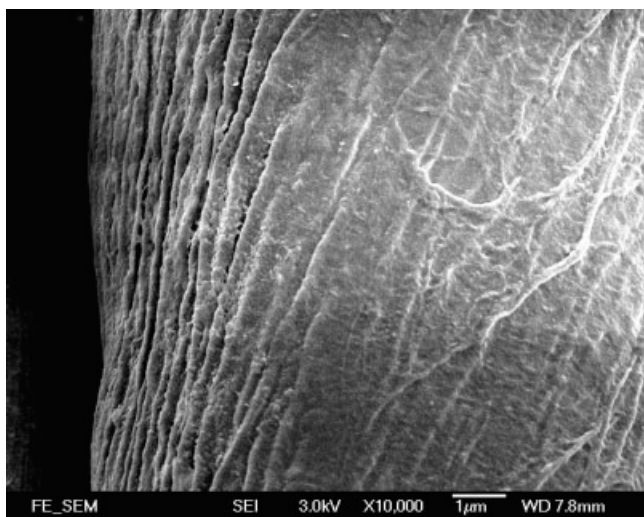


Figure 4 LTP-treated fabric (2 min treatment) without pretreatment paste coating ($\times 10,000$).

system. As a result, development of cracks was found along the fiber axis.¹⁵

Figure 5 shows clearly the untreated cotton fabric surface padded with pretreatment paste coating, which adhered on the fiber in the form of a web. This fiber surface was much rougher than the one without pretreatment paste coating as shown in Figure 3. Figure 6 shows that the LTP-treated cotton fabric padded with pretreatment paste coating had a better surface smoothness when compared with the LTP-treated sample as shown in Figure 4. The surface appearance revealed that during the padding of pretreatment paste, the cracks so formed on the fiber surface after the LTP treatment were filled up and encased with the pretreatment paste. In addition, with the formation of cracks on the fiber surface, the

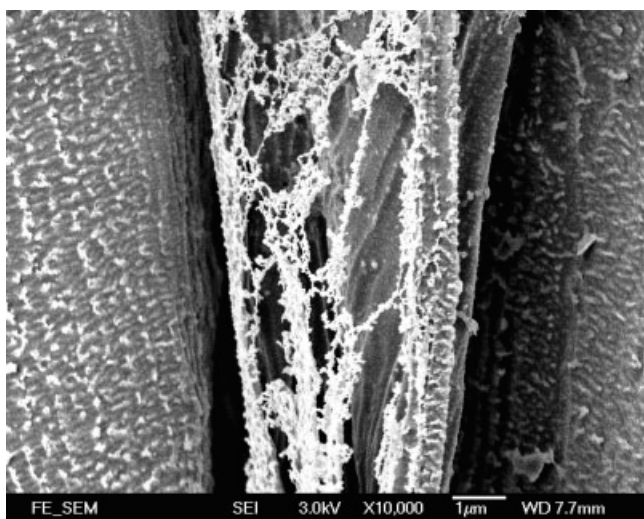


Figure 5 Untreated fabric with pretreatment paste coating ($\times 10,000$).

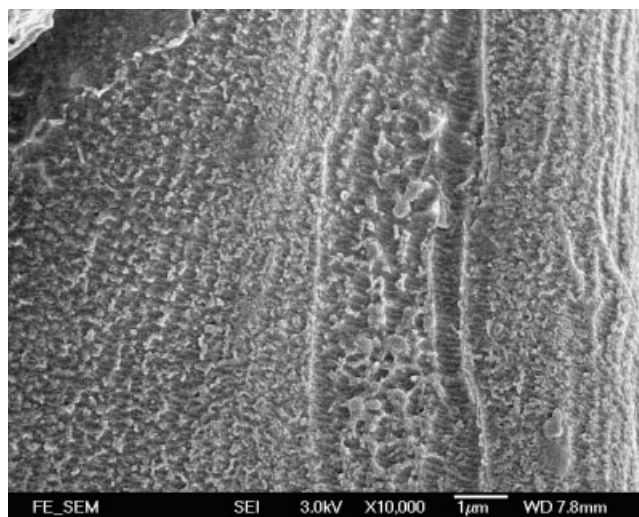


Figure 6 LTP-treated fabric (2 min treatment) with pretreatment paste coating ($\times 10,000$).

surface area of fiber would be increased accordingly, thereby facilitating more dyes to approach the fiber surface and increase the uptake of dye consequently.

Color-fastness test

The color-fastness results to light, washing, and crocking of the printed fabrics are given in Table I. The results showed that the color fastness of ink-jet-printed cotton fabric with the LTP pretreatment achieved better color-fastness properties than the untreated cotton fabric. Of the different LTP-treatment exposure times being studied, it was observed that better maximum color fastness could be achieved at 2 and 5 min of LTP exposure times when compared with the prolonged exposure times, i.e., 15–60 min. The changes in color fastness with respect to prolonged LTP exposure time might be due to the improvement of moisture-absorption properties of

TABLE I
Different Color-Fastness Properties
of the Printed Cotton Fabric

Sample	Light	Washing		Crocking	
		Staining on multifibre fabric ^a	Colour change	Wet	Dry
Control	2–3	4	4	3	4
1 min	3	4	4	3–4	4
2 min	3–4	4–5	4–5	4	4–5
5 min	3–4	4–5	4–5	4	4–5
15 min	3–4	4–5	4–5	3–4	4
30 min	3	4	4	3–4	4
60 min	3	4	4	3–4	4

^a The fibre components in the multifibre fabric included wool, acrylic, polyester, nylon, cotton, and acetate.

TABLE II
Outline Sharpness of Ink-Jet-Printed Fabrics

Sample	Sharpness	
	Warp (mm)	Weft (mm)
Control	82	81
1 min	81.5	81
2 min	81	80
5 min	81	80
15 min	81.5	80.5
30 min	81.5	81
60 min	81.5	81

cotton fabric, i.e., enhancement of hydrophilic groups in the cotton fiber,¹¹ resulting in more moisture being absorbed during the steam fixation process. This would eventually cause the hydrolysis of reactive dye in the printing ink, leading to a slight reduction in the color-fastness results. Although the color-fastness properties of 2 and 5 min LTP-treated fabrics were the same, yet the color yield of 2 min LTP-treated fabric is better than that of 5 min when compared.

Outline sharpness of the ink-jet-printed fabric

The outline sharpness of the ink-jet-printed pattern was measured by the optical analysis method, with the results being shown in Table II. Obviously, the ink-jet-printed patterns in warp direction were thicker than those in weft direction for both the untreated and LTP-treated fabrics. This might be due to the differential wicking effect caused by the warp and weft yarns. When comparing the width of the printed patterns, the patterns printed on the LTP-treated cotton fabrics were narrower than the untreated fabric in both warp and weft directions. This could be attributed to the reduced spreading of the printed reactive inks as a result of the strong fiber and dye attraction, i.e., formation of covalent bonding between the hydroxyl group of fiber¹¹ and the reacting system of the reactive dye present in the printing ink. Consequently, the LTP treatment on cotton fabric could enhance the outline sharpness of the ink-jet prints.

CONCLUSIONS

This article was aimed at studying the effect of LTP treatment on the cotton fabric prior to digital ink-jet printing. Before padding the pretreatment paste containing sodium alginate onto the cotton fabric, the cotton fabrics were exposed to different durations of

LTP with oxygen gas as the plasma medium. It was found that the LTP-treated cotton fabric surface turned yellow when compared with that of untreated cotton fabric. However, there was no further enhancement of yellowness after 2 min of LTP exposure time. After padding the pretreatment paste onto the LTP-treated cotton fabrics, the yellowness index was further enhanced due to the fact that the color of sodium alginate was yellow in nature.

With the assistance of LTP treatment, the final color yield of the ink-jet-printed cotton fabrics was improved significantly, with maximum color yield being obtained at 2 min of LTP exposure time but decreased at prolonged exposure time.

SEM pictures showed that the LTP treatment could facilitate the filling up of fiber cracks with pretreatment paste, which would in turn increase the fiber surface area. Hence, more dyes could approach the fiber surface during the ink-jet printing process, leading to the dye uptake subsequently.

It was obvious that not only the dye uptake was increased after the LTP treatment, but the color-fastness properties and the definition of the final print marks were also improved. On the whole, it was concluded that coupling of LTP treatment together with the ink-jet printing technique could make the printing process more effective.

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