(REFEREED RESEARCH)

THE INFLUENCE OF RHEOLOGICAL PROPERTIES OF THE PRETREATMENT THICKENERS ON INK-JET PRINTING QUALITY

İNK-JET BASKIDA ÖN İŞLEM KIVAMLAŞTIRICILARININ REOLOJİK ÖZELLİKLERİNİN BASKI KALİTESİNE ETKİSİ

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ABSTRACT

Pretreatment process is very important for ink jet printing system. Pretreatment solutions that is transferred to the cotton fabric before reactive ink-jet printing affects printing quality. In this study, the influence of the rheological properties of pretreatment thickeners on printing quality and color yield has been researched. The reological properties of the pretreatment sollution is determined mainly by the rheological properties of the thickener that is used. The influence of the rheological properties of the pretreatment sollutions which is prepared with different kind of thickeners at different concentrations, on paste add-on, penetration and colour yield values is investigated. As a result, it was observed in this study that at applied conditions the rheological properties of the pretreatment pastes applied have not a significant influence on color yield and ink-jet printing quality.

Key Words: Ink-jet printing, Rheological properties, Thickeners.

ÖZET

Inkjet baskı sisteminde ön işlem prosesi büyük önem taşımaktadır. Pamuklu kumaşların reaktif inkjet baskı işlemi öncesinde kumaşlara aktarılan ön işlem patları baskı kalitesini etkilemektedir. Bu çalışmada, ön işlem kıvamlaştırıcılarının reolojik özelliklerinin baskı kalitesi ve renk verimine etkisi araştırılmıştır. Ön işlem patlarının reolojik özelliklerini büyük ölçüde kullanılan kıvamlaştırıcının reolojik özellikleri belirlemektedir. Farklı türde kıvamlaştırıcılarla farklı konsantrasyonlarda hazırlanan ön işlem patlarının reolojik özelliklerinin aktarılan pat miktarı, penetrasyon oranları ve renk verimleri üzerine etkisi incelenmiştir. Bu çalışmada sonuç olarak uygulanan koşullarda ink-jet baskıda ön işlem patlarının reolojik özelliklerinin renk verimi ve baskı kalitesine önemli bir etkisinin olmadığı ortaya konulmuştur.

Anahtar Kelimeler: İnk-jet baskı, Reolojik özellikler, Kıvamlaştırıcılar.

1. INTRODUCTION

Textile printing can be best described as the art and science of decorating a fabric with a colorful pattern or design (1). At today's textile world, costumer requirements are changing rapidly, collections renew in two months. Textile products must have different appearance or functional properties, and textiles must be produced by environmental production process to be preferred (2). Total production of textile prints approaches 19 linear billion meters of fabric per year and shows an average growth rate of the order of 2% per year (3). Today the majority of all textiles which are printed using rotary screen print machines. While this technology offers high speed and low product cost, there are many drawbacks. The world of textile printing is rapidly changing and digital textile printing technology supports the industrial trends: integration in a digital workflow, qualitative and short runs, fast turnaround orders, reduced stock risks, exclusive, unique designs and personalized textile, demanding an ability to supply rapidly. However, due to its inherently slow application speed, the digital printing process has yet to be adopted and successfully used as a component for full-scale production (4). On the other hand digital printing technologies are considerably cleaner than conventional ways of applying color to textiles (5).

Rheology is the science of deformation and flow (6). Newton was the first scientist who studied on rheology in

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the seventeenth century. He was proved that all fluids that have basic structure have a constant friction resistance against the flow. This internal resistance is described as viscosity by Newton. To characterize rheological behavior of materials Newton needed first to define some terms. Consider a liquid that is subjected to a shearing force as seen in Figure 1 (7).

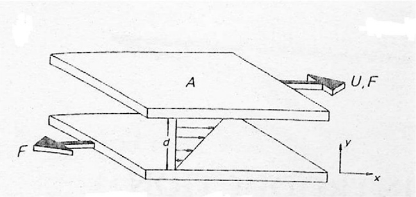

Figure 1. Newton's flow theorem (7)

The material has a thickness *d*, and assume that the layer at the bottom is stationary and the layer at the top is movable. Due to the stress, the upper layer is displaced. The pulling action is the shear stress(τ), which is defined as the force F over the area A.

$$\tau = F/A \qquad (1)$$

If the flow is laminar, the maximum flow rate will be at the top layer and the minimum flow rate will be at the bottom layer in proportion with the arrows in the figure. If top layer is moving at a velocity *U*, the velocity gradient is defined as the shear rate (*D*).

$$D = U/d \qquad (2)$$

And the stress is related directly to the shear rate:

$$\tau = \eta . D \qquad (3)$$

The coefficient η in this equation is a measure of the resistance of the material flow, that is, its viscosity. The units of shear stress (τ) is N/m^2 or Pascal, shear rate (D) is s^{-1}, and viscosity (η) is poise or Pa.s (8).

According to Newton, viscosity is independent of the shear rate, which is true only for ideal, Newtonian fluids such as water and glycerin. There are many fluids which don't fit Newton's equation which are called Non-Newtonian fluids. Their viscosity is not constant and changes as a function of shear rate. Many fluids show a decrease in viscosity as shear rate increase (Pseudoplastic flow). Some fluids show an increase in viscosity as shear rate increase (Dilatant flow). Thickeners used in textile printing generally show pseudoplastic (shear thinning) flow behavior. When these are subjected to shear stress, H-bridges and Van der Waals forces in their structure break and the internal friction decrease that result in lower viscosity (9).

The fluidity is another term about rheology. Fluidity index is the numerical value of fluidity. Liquids having pseudoplastic flow properties conform to the empirical model of Oswald.

$$\tau = k.D^n \qquad (4)$$

where, τ is the shear stress (D/cm^2), k is the consistency index (cP), D is the shear rate (s^{-1}) and n is the flow index. As flow index increase and approaches 1, the liquid shows more Newtonian behavior.

In conventional cotton printing with reactive dyes, the printing paste contains reactive dyes, thickeners, alkali, urea and oxidizing agent. The rheological properties of the printing pastes are principally determined by thickeners because 60% of the printing paste consists of the thickener. Success of a printing process is established by the sharpness of mark, levelness, correct color, good hand and high fastness which are directly influenced by the rheology of the thickener (9). After printing, fixation and washing process is applied to the fabric.

In digital printing, process steps are different. Before digital printing, a pretreatment solution which includes auxiliary agents but not the reactive dye, has to be applied to the fabric. After pretreatment the fabric is printed digitally and then fixation and washing process is applied to the fabric.

Print paste rheology is a key word for printing quality. It affects color, sharpness of mark, levelness, hand, and color yield at conventional printing (10). The purpose of this study is to find out if the rheological properties of the pretreatment solution effect the digital printing quality.

2. MATERIAL AND METHOD

3.2. Material

100 % cotton, woven fabric (120 g/m^2, Ne 67/1) was used for all printing process. Protex LV (low viscosity alginate-LVA, Prochem), Protex HV (high viscosity alginate-HVA, Prochem) and Asel TD 60 (carboxymethyl cellulose-CMC, Acıselsan) were used as thickener. Sodium bicarbonate (Smyras) as alkali, Ludigol (sodium meta-nitrobenzene sulfonate, BASF) as oxidizing agent and urea (Smyras) were used.

3.2. Method

Trials were performed according to the experiment plan which was composed with the help of factorial experimental design and repeated three times. Effects of two factors on printing quality were analyzed. Factors and their levels are shown in Table 1. The thickener stock paste concentrations are shown in Table 2.

Table 1. Factors and their levels used at trials

LEVELS	FACTORS	
	Thickener Type	**Thickener Concentration**
1	High viscosity alginate	Low
2	Low viscosity alginate	Medium
3	Carboxymethyl cellulose	High

Table 2. Thickener stock paste concentrations

Thickener type	Thickener concentrationslevels and values (%)		
	Low	**Medium**	**High**
High viscose alginate	3%	4%	5%
Low viscose alginate	7%	8%	9%
Carboxymethyl cellulose	8%	10%	12%

On the other hand, to compare the rheological properties of thickeners, all of them were prepared at 4%, 5%, and 6% concentration. Thickener stock pastes were prepared with soft water on a laboratory type mixer and they were allowed to stand for 24 hours to complete swelling.

After that, pretreatment solutions were prepared according to Table 3 by stirring for 30 minutes, and the total weight of each container was 150 g.

Table 3 Pretreatment solution ingredients

Thickener	300 g
Sodium bicarbonate	20 g
Ludigol	10 g
Urea	25 g
Water	655 g
Total	**1000 g**

The rheological properties of the thickeners and pretreatment solutions were measured (coaxial cylinder geometry) by using a Brookfield DV-III Rheometer at increasing and decreasing shear rates. Rheological measurements were evaluated by equation 4 with the aid of the paste analysis equation (Eq. 5). The shear sensitivity factor value of pastes can be calculated by equation 5.

$$\eta = k' R^{n'} \qquad (5)$$

where, η is the viscosity (cP), *k′* is the consistency multiplier, *R* is rotational speed (rpm) and *n′* is the shear sensitivity factor.

Pretreatment solutions were transferred to the fabrics by padding and screen printing. Padding process was applied by a padding machine (Ernst Benz LFV.350/2 RFA modal) On the other hand, pretreatment solutions were transferred to the fabrics by using a laboratory type printing machine (Zimmer MDK) with 70 mesh 100% PA printing screens, 10 mm squeegee at 4 m/min speed, and grade 5 pressure. The screen pattern was 20*30 cm^2 flat pattern.

Pretreated fabrics were weighed immediately and applied paste amount (paste add-on) was calculated by equation 6.

$$\text{Paste add-on} = \frac{(E_2 - E_1)}{A} \qquad (6)$$

The unit of paste add-on is g/m^2, E_1 (g) is the weight of the fabric before pretreatment, E_2 (g) is the weight of the fabric after pretreatment, *A* (m^2) is the area that pretreatment solution is transferred. After pretreatment, samples were dried in a laboratory type drying machine (Ataç GK 40) at 100 ºC for 2 minutes before ink-jet printing. The ink-jet printer was Mimaki TX3 – 1600. Ink-jet printing was applied at 720x720 dpi resolution, and the printing color was magenta (RGB: 255, 0, 255).

After printing, patterns were dried and samples put into the steamer to be steamed with superheated steam at 102 °C for 10 minutes for color fixation. Samples were washed for 5 minutes at 25 °C, 10 minutes at 100 °C, 5 minutes at 70 °C, 5 minutes at 40 °C and 5 minutes at 25 °C. At the end of the process samples were dried.

Color measurements were made on a Hunter Lab ColorQuest II spectrophotometer. K/S values were calculated at the maximum absorption wavelength. The percent penetration values of the thickeners were determined by Equation 7.

$$\text{Penetration \%} = \frac{(K/S)_b}{0.5\left[(K/S)_f + (K/S)_b\right]} \qquad (7)$$

$(K/S)_f$ and $(K/S)_b$ are the K/S values of the front and back side respectively.

Color difference values (ΔE) of the samples were calculated by the Equation 8. Color values of the sample that was pretreated by the solution which contained 3 % high viscosity alginate stock pastes, was assumed as the standard. In literature, if ΔE value is lower than 1, it’s assumed that there is no color difference between the samples.

ΔE=[(ΔL*)2+(Δa*)2+(Δb*)2]1/2 (8)

In the equation ΔE is the color difference value, L* is the brightness value, a* is red/green color value, b* is yellow/blue color value.

To calculate the mark sharpness values numerically, the printing pattern had 1 mm thick lines through warp and weft direction. 100 times zoomed in pictures of printed samples was copied to the computer by a stereomicroscope and the last thickness of lines were measured.

The handle of the printed samples was evaluated subjectively. 15 people touched printed samples and evaluate the handle according to the evaluation points. Average of evaluation points was calculated and used. According to the evaluation points; 1 very stiff, 2 stiff, 3 medium handle, 4 soft, 5 very soft.

3. RESULT AND DISCUSSIONS

3.2. Rheology

Rheological properties of thickeners are closely related to the chemical structure of the thickener, its concentration and interaction with other components (11). Figure 2 shows that the flow index of carboxymethyl cellulose was higher than the other thickeners at all concentrations. When we compare high viscosity alginate and low viscosity alginate, they almost showed the same flow index at 4% and 5% concentration. At 6% concentration high viscosity alginate lost its fluidity.

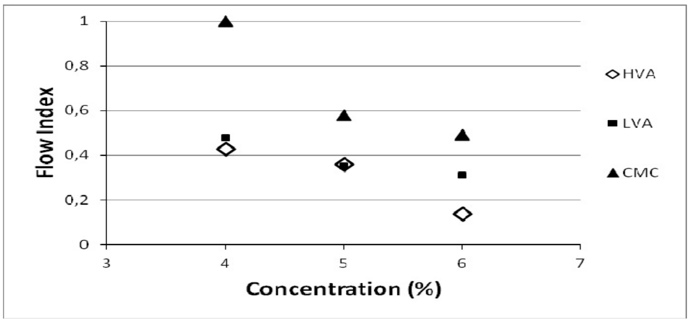

Figure 2. Flow index of high viscosity alginate, low viscosity alginate and carboxymethyl cellulose

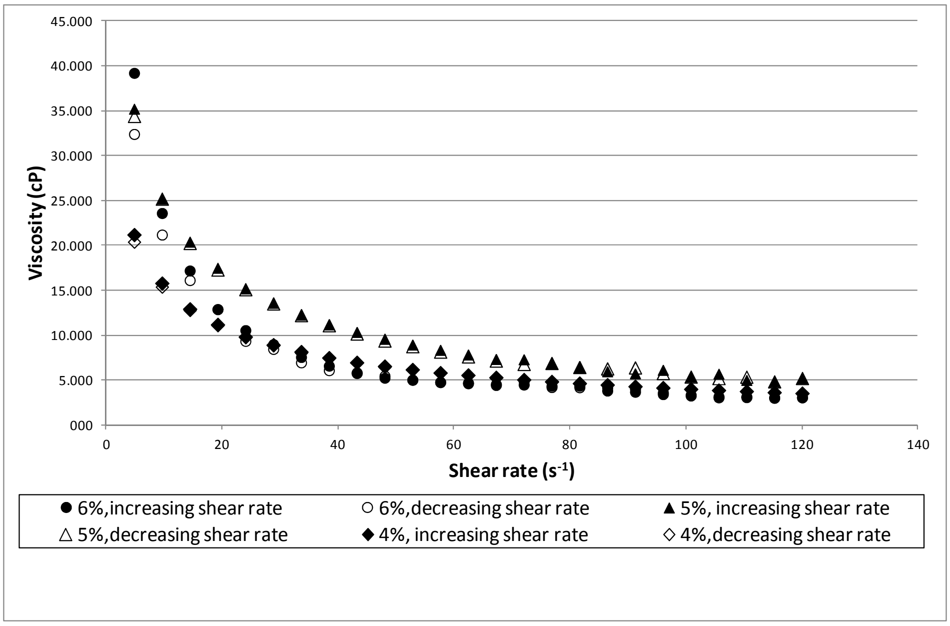

Figure 3. Viscosity profile of high viscosity alginate

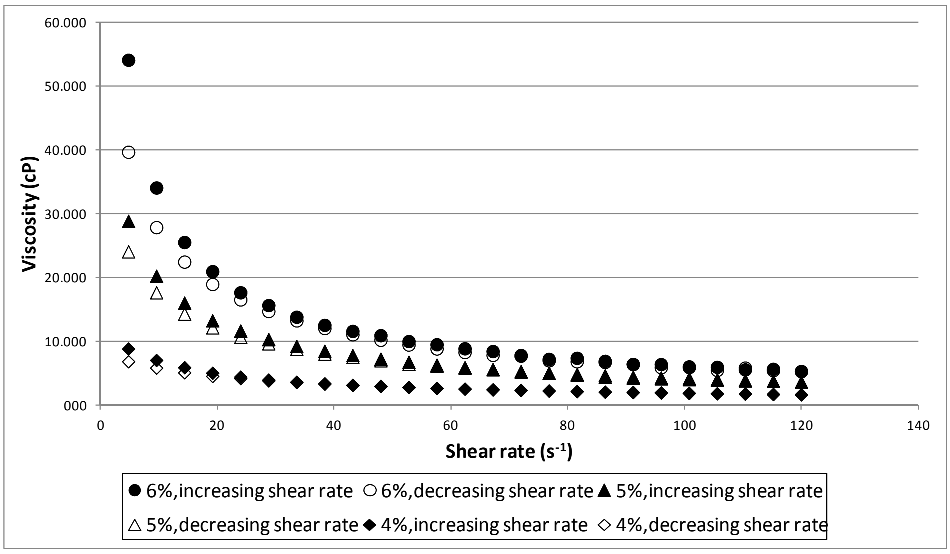

Figure 4. Viscosity profile of low viscosity alginate

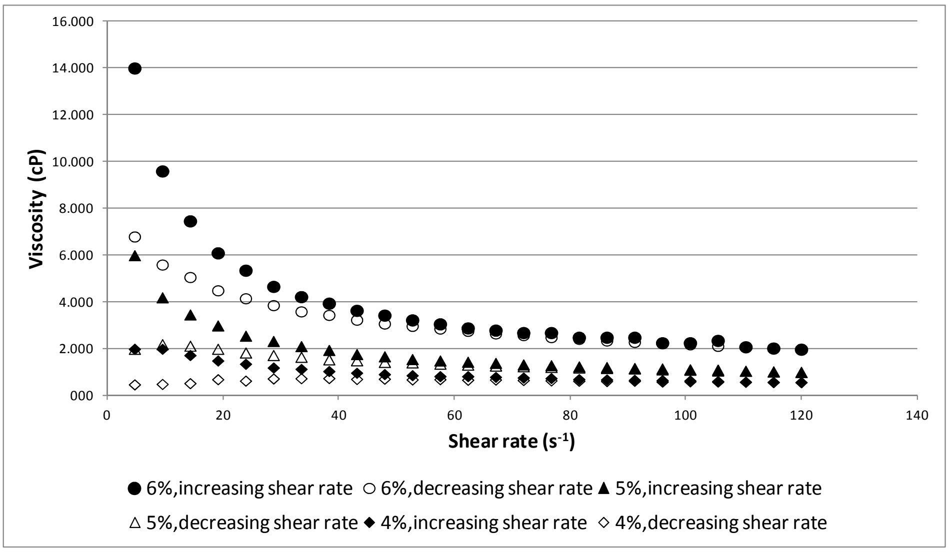

Figure 5. Viscosity profile of carboxymethyl cellulose

All thickeners were pseudoplastic (the viscosity decreased with increasing shear rate). On the other hand, differences between increasing and decreasing shear rate curves were observed for low viscosity alginate and carboxymethyl cellulose, especially at low shear rates (Fig. 4 and 5) this indicates thixotropy. A thixotropic fluid shows a slow return to the original apparent viscosity after shear thinning affected flow.

The rheological curves of the thickeners are shown in Fig. 6, 7 and 8. For all thickeners the applied shear force increased as the concentration increased and reached 10.000 D/cm^2 at 6% concentration of high viscosity alginate. Shear force values of other thickeners at 6% concentration were 7000 D/cm^2 and 2500 D/cm^2. This indicates that the pseudoplastic property of high viscosity alginate at these concentrations increased more.

Flow index and shear sensitivity values of pretreatment solutions that were prepared with thickeners at medium concentration are shown in Table 4. Flow index of the pretreatment solutions are listed as HVA < CMC < LVA, as it can be seen from Table 4. On the other hand, for shear sensitivity the order is LVAL < CMC < HVA.

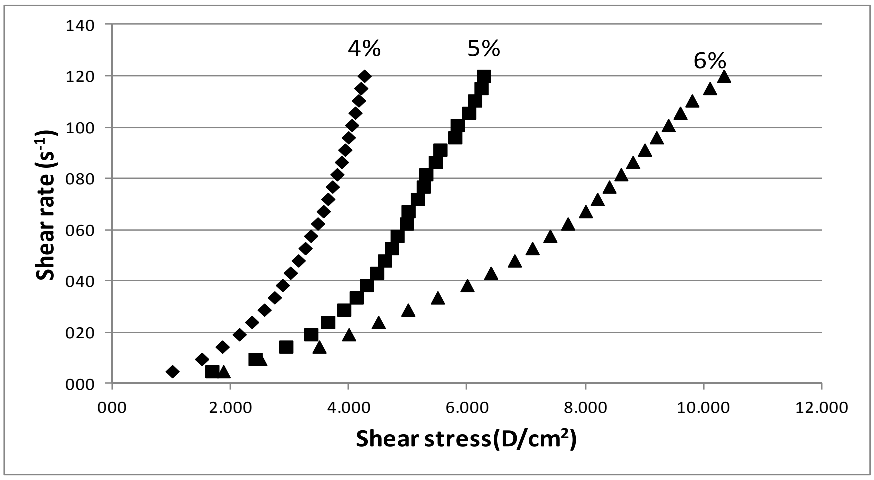

Figure 6. Rheological curve of high viscosity alginate

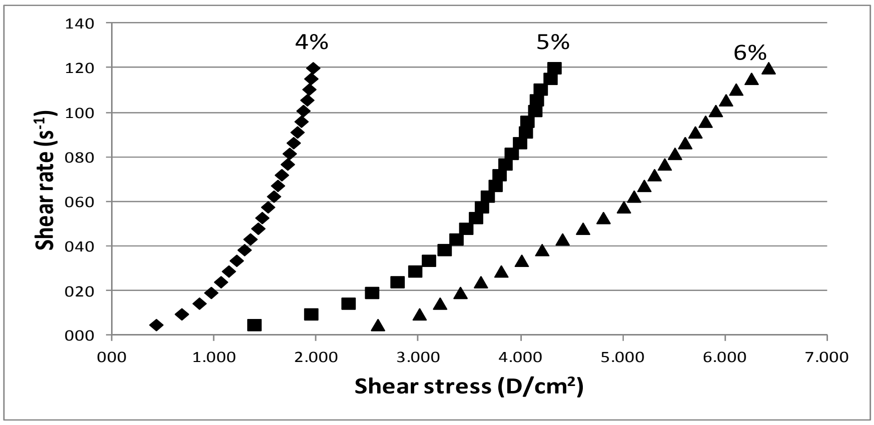

Figure 7. Rheological curve of low viscosity alginate

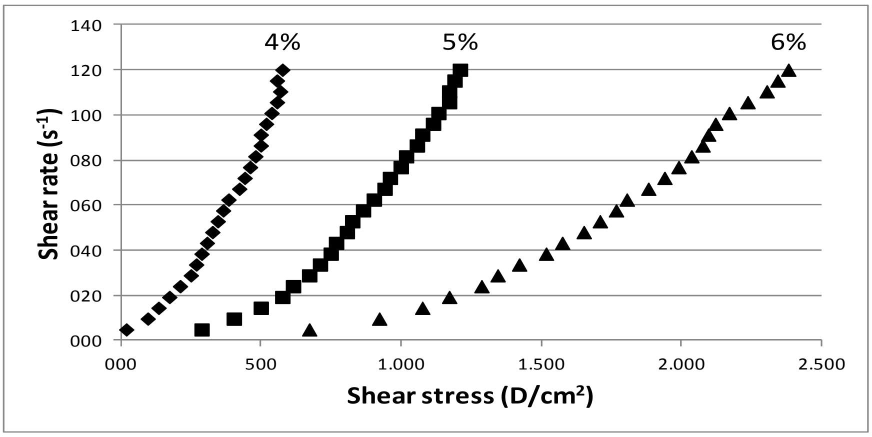

Figure 8. Rheological curve of carboxymethyl cellulose

Table 4. Flow index and shear sensitivity values of pretreatment solutions

Thickener Type(%)	**Flow Index**	**Shear Sensitivity**
High Viscosity Alginate (%4)	0,89	0,11
Low Viscosity Alginate (%8)	0,59	0,41
Carboxymethyl Cellulose (%10)	0,69	0,31

3.2. Printing quality parameters

The result of printing is determined by printing quality and repeatability, printing quality is determined by printing efficiency, smoothness, mark sharpness and penetration [10]. Figure 9 shows paste add on, penetration and K/S values of fabrics which were pretreated by padding. For all thickeners as the concentration of the thickener increased, amount of paste add on decreased. It can be said that the flow index of the thickeners decreased by increased concentration so the fluidity decreased and the amount of paste add on tended to decrease. But the difference between paste add on amounts was maximum 40 gram per meter and this value doesn't affect the printing quality practically. At applied conditions, rheological properties of pretreatment solutions didn't affect amount of paste add-on significantly.

Penetration and K/S values of printed fabrics are very close to each other. As it's seen from ΔE values of back sides of printed fabrics in Table 5, thickener type and concentration didn't affect the penetration significantly. ΔE values of front side of printed samples are shown in Table 5. All ΔE values were lower than 1, so colors of printed samples were visually indistinguishable. As a result, it can be said that thickener type and concentration didn't affect the color yield significantly.

Figure 10 shows paste add on, penetration and K/S values of fabrics which were pretreated by screen printing. For all thickeners, as concentration of the thickener increased, amount of paste add on tended to decrease. But the difference between paste add on amounts was maximum 20 gram per meter and this value doesn't affect the printing quality practically. It can be said that at applied conditions, rheological properties of pretreatment solutions, thickener type and concentration didn't affect amount of paste add-on significantly.

Penetration and K/S values of printed fabrics were very close to each other. As it's seen from ΔE values of back and front sides of printed fabrics in Table 7, thickener type and concentration didn't affect the penetration and color yield significantly. All ΔE values were lower than 1, so colors of printed samples were visually indistinguishable.

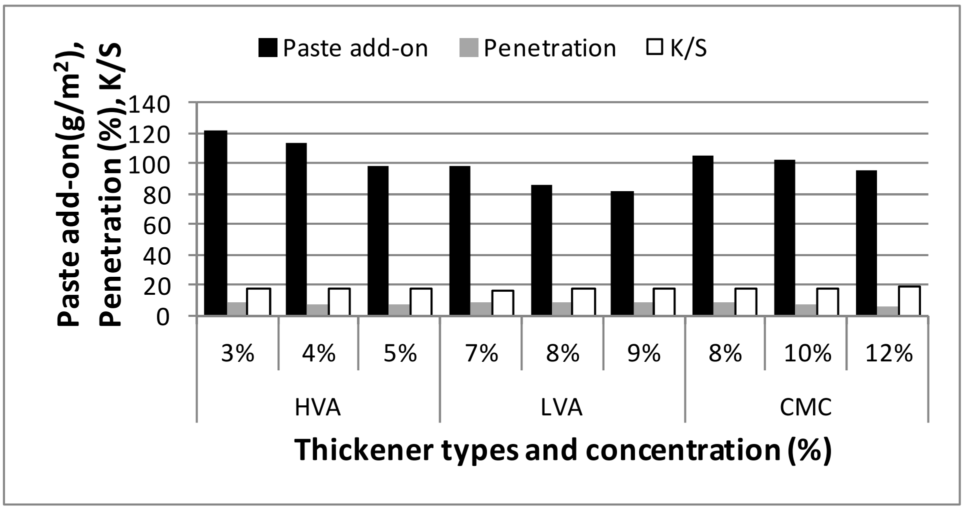

Figure 9. Paste add-on, penetration, and K/S values of the samples that is pretreated by padding

Table 5. ΔE values of back and front sides of printed samples

Thickener Type	Concentration	ΔE values of back sides	ΔE values of front sides
HVA	4%	0,71	0,33
	5%	0,65	0,27
LVA	7%	0,78	0.98
	8%	0,82	0,45
	9%	0,95	0,8
CMC	8%	0,56	0,21
	10%	0,69	0,68
	12%	0,77	0,95

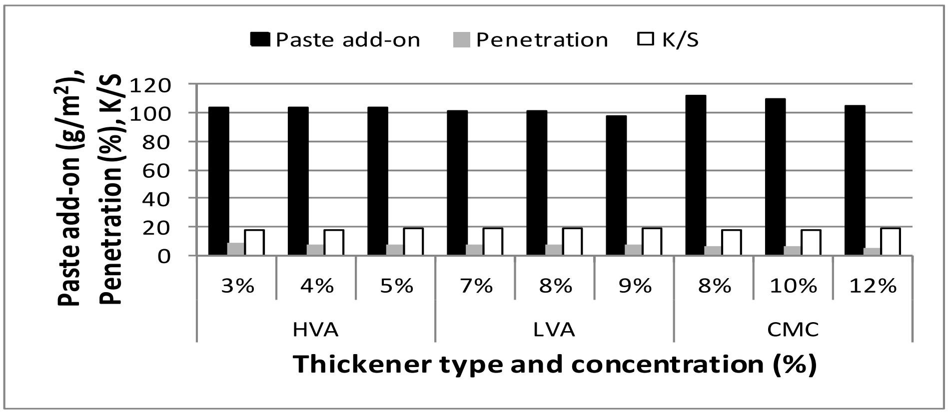

Figure 10. Paste add-on, penetration, and K/S values of the samples that is pretreated by screen printing

Table 6. ΔE values of back and front sides of printed samples

Thickener Type	Concentration	ΔE values of back sides	ΔE values of front sides
HVA	4%	0,72	0,75
	5%	0,96	0,85
LVA	7%	0,78	0,9
	8%	0,93	0,94
	9%	0,88	0,97
CMC	8%	0,69	0,38
	10%	0,82	0,69
	12%	0,98	0,92

Mark sharpness is measured numerically as it's explained before and values are shown in Figure 11 and 12.

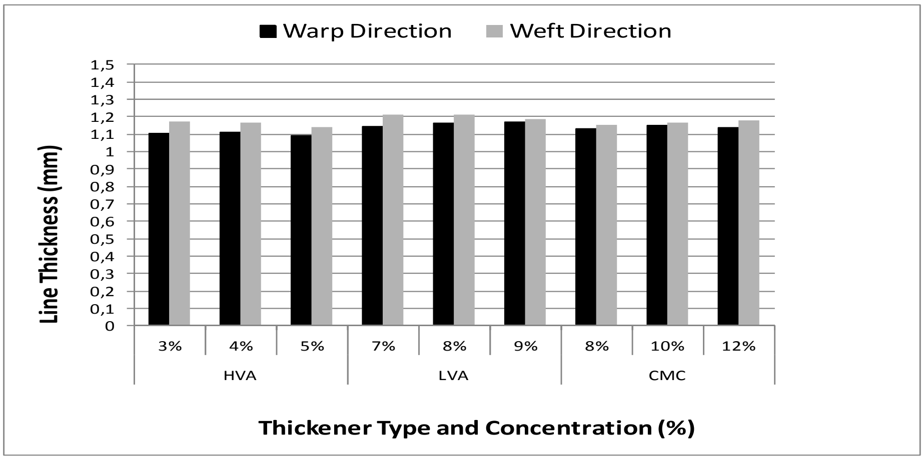

Figure 11. Mark sharpness of the samples which is pretreated by padding

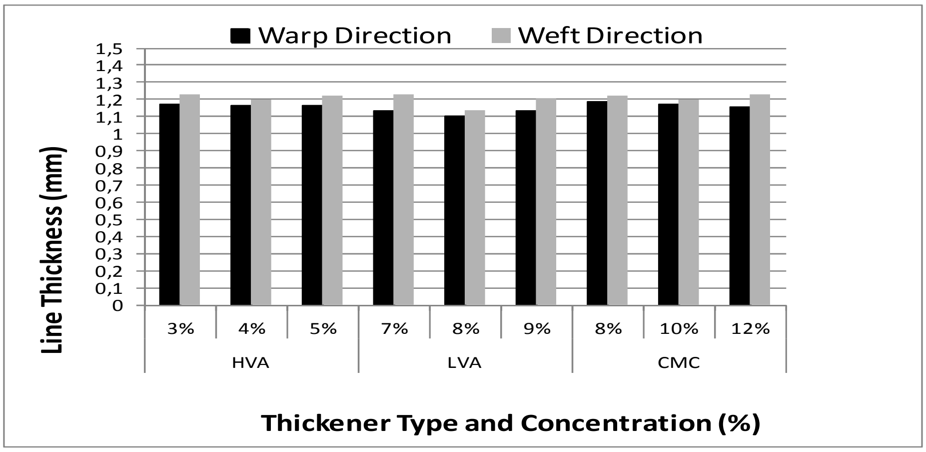

Figure 12. Mark sharpness of the samples which is pretreated by screen printing

Thickener type and concentration didn’t have a significant effect to thickness of the lines which were printed through the warp and the weft direction for both padding and screen printing. But for all samples, the spread of printings through the warp direction is more.

Evaluation of handle was done subjectively. Values of the handle of printed samples are shown in Table 8. As it’s seen from the table, handle of printed samples were undistinguished.

4. CONCLUSIONS

Experiments were examined at 3 levels of thickener concentration and thickener type and it’s very possible that at different concentrations and conditions other conclusions might be drawn.

In conventional printing, the rheological behavior of printing pastes affects the printing quality significantly (9, 11 and 13) because reactive dye is contained in the printing paste. The dye molecules flow and move in the fabric capillary with the printing paste. But in ink-jet printing the pretreatment solution doesn’t have reactive dye in. Pretreated fabrics are dried and then they are printed with ink-jet printers. When the pretreatment solution dries, we can’t mention about flow properties and rheology of thickeners.

It can be said that at applied conditions, rheological properties of thickener and pretreatment solutions didn’t affect color yield, penetration, amount of paste add-on, mark sharpness and handling. The cost of carboxymethyl cellulose thickener is lower than other thickeners and the printing quality is almost same. In reactive ink-jet printing, carboxymethyl cellulose is advised to be used as pretreatment thickener.

Table 7. The handle values of printing samples

Kıvamlaştırıcı Türü	Concentration	Handle values (Padding)	Handle Values(Screen printing)
Y.V.A	3%	4-5	4-5
	4%	4	4
	5%	4	4
D.V.A	7%	4	4
	8%	4	4
	9%	3-4	4
C.M.C	8%	4	4
	10%	4	4
	12%	3-4	3-4

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