(REFEREED RESEARCH)

A STUDY ON THE PROCESS PARAMETERS OF DISCHARGE PRINTING OF COTTON FABRICS

PAMUKLU KUMAŞLARIN AŞINDIRMA BASKISINDA İŞLEM PARAMETRELERİ ÜZERİNE BİR ÇALIŞMA

Arzu ÖZERDEM YAVAŞ[1], Arif Taner ÖZGÜNEY[2]*, Ahmet ÇAY[2], Burçin ESER[2]

[1]Pamukkale University, Department of Textile Engineering, Denizli, Turkey
[2]Ege University, Department of Textile Engineering, İzmir, Turkey

Received: 23.03.2011 Accepted: 03.10.2011

ABSTRACT

Discharge printing of cotton fabrics with sodium- and zinc formaldehyde sulphoxylate with different fixation conditions was discussed in this study. Superheated steam, saturated steam and thermofixation were used for fixation processes. It was observed that steam based fixations resulted in the higher discharging effects, while thermofixation lead to an inadequate effect even in higher temperatures. Superheated steam was found to be advantageous in terms of lower fixation times. Sodium formaldehyde sulphoxylate gave superior discharging effects compared with zinc formaldehyde sulphoxylate, which caused higher strength loss especially in superheated steam fixation. Furthermore, the effects of the softeners on the discharge printing results were also investigated in the scope of the study.

Key Words: Discharge printing, Fixation, Strength loss, Softeners.

ÖZET

Bu çalışmada, pamuklu kumaşların sodyum formaldehit sülfoksilat ve çinko formaldehit sülfoksilat ile farklı fikse şartlarında aşındırma baskısı ele alınmıştır. Fikse işlemleri için kızgın buhar, doymuş buhar ve termofiksaj kullanılmıştır. Buhar bazlı fiksaj işlemlerinin daha iyi aşındırma etkileri sağlarken, termofiksaj işleminin yüksek sıcaklıklarda dahi yetersiz etki oluşturduğu gözlemlenmiştir. Kızgın buhar, daha düşük işlem süresi nedeniyle avantajlı bulunmuştur. Sodyum formaldehit sülfoksilat, çinko formaldehit sülfoksilata nazaran daha iyi aşındırma etkileri sağlamıştır. Çinko formaldehit sülfoksilat ile aşındırma baskıda daha yüksek mukavemet kayıpları görülmüştür ve bu kayıp en çok kızgın buharla işlem sonrası ortaya çıkmıştır. Buna ilaveten, yumuşatıcıların aşındırma baskı sonuçlarına etkisi de çalışma kapsamında incelenmiştir.

Anahtar Kelimeler: Aşındırma baskı, Fiksaj, Mukavemet kaybı, Yumuşatıcılar.

1. INTRODUCTION

Special printing applications by screen printing are of great importance with the increased concernment of small lot production and fashion related products due to the severe competitive conditions of the textile industry. Discharge printing method is one of the popular techniques in these applications due to the aesthetic attractiveness (1).

The main principle of discharge printing is the degradation of the chromophore group of the dye (2). Process involves the dyeing of the fabric with a dischargeable dye or a dye combination and then the printing of the fabric with a paste including discharging agent that destroys the color in designed areas (3). Discharge printing classified into two groups, such as white discharge in which the paste contains only the discharging agent; and colored discharge where a discharge resistant (illuminating) dye is mixed with the discharging paste (4).

The most widely used reducing agents are the formaldehyde sulphoxylates. Sodium formaldehyde sulphoxylate has been used widely in many years and other products are the zinc formaldehyde sulphoxylates, calcium formaldehyde sulphoxylates (5). Sodium formaldehyde sulphoxylate develops its full redox potential in the alkaline pH range (6), thus in practical, it is used for white discharges or vat discharges on cotton. On the other hand, zinc formaldehyde sulphoxylate is suitable for white or pigment discharges due to the compatibility with acidic medium.

Dischargeability of a dyestuff is mainly deals with its chemical structure, and the presence of an azo group is the most important requirement (7). On the other hand, Dowson and Hawkyard reported that many reactive dyes did

---

* Corresponding Author: Arif T. Özguney, arif.taner.ozguney@ege.edu.tr, Tel. +90 232 3112786, Fax.+90 232 3399222

not discharge to a good white because an amine moiety of the dye remains chemically attached to the fiber (1).

The impurities or chemicals in the fabrics can have a negative impact on dischargeability. However, since discharge prints are mainly used for the piece goods such as t-shirts as a final process, the fabrics generally includes softeners before the printing process. Thus the effects of the softeners on the discharging effect should be discussed. Textile softeners are used to improve the handle of fabrics, since many textiles require softer and smoother handle (7) and they are used in nearly every finishing formulation (8). Together with the improved handle, they may also serve to improve the processability and wear characteristics of the textiles (7). Besides many advantages, softeners results in some problems in screen (garment) printing processes, especially due to the fixation step. Özgüney and Özkaya (9) investigated that softeners lead to a higher yellowing during the fixation step both in bleached and dyed samples. They emphasized that the use of cationic and amino-functional based silicon softeners should be abstained. Since the discharge printing involves fixation step, the effects of the softeners on the discharging efficiency were also concerned in this study.

The fixation of the discharge prints can be carried out by steaming or thermofixation methods. Both of these methods may be used for white discharges, however steaming for vat discharges and thermofixation for pigment discharges are dispensable. The quality of the product depends on the temperature and moisture content of the fixation process and any error will cause destruction of the material (2), thus the effects of the fixation methods and conditions on both discharging efficiency and quality should be systematically determined and optimized. Therefore, in this study the effects of fixation methods for several discharging agents were compared and an expressive research was conducted to determine the improvement possibilities and limitations in discharge printing of cotton fabrics.

2. MATERIAL AND METHOD

A single jersey knitted cotton fabric weighting 169 g/m^2 was used in this study. The fabric was dyed by a combination of three dischargeable dyes, (%1 owf CI Reactive Yellow 176, %1 owf CI Reactive Red 239 and %7 owf CI Reactive Black 5) in a jet dyeing machine.

The dyed cotton fabric was printed with white discharge printing pastes of the compositions given in Table 1. Setagum VAT 80 (Setaş Kimya, Turkey) was selected as thickener which is a derivate of starch ether. In order to conduct the effects of the reducing agent type, two types of reducing agents such as sodium formaldehyde sulphoxylate (CI Reducing Agent 2) and zinc formaldehyde sulphoxylate (CI Reducing Agent 6) were used. Both neutral and alkaline printing pastes were adjusted for sodium formaldehyde sulphoxylate, and the effects of the concentration of the reducing agents were also investigated. The viscosities of the pastes were adjusted to be 7-8 poise with a Brookfield viscosimeter. The discharge printing was carried out on a J. Zimmer MDK (J Zimmer Maschinenbau GmbH, Austria) laboratory scale printing machine with 70 Nr polyester (PES) gauze template at 4 m/ min at press 5 of pressure and a doctor blade in 10 mm diameter. After printing, fabrics were dried at 100 ^{o}C for 2 min.

The samples were fixated by thermofixation, saturated steam fixation and superheated steam fixation. Fixation conditions are given in Table 2. Thermofixation was carried out with a laboratory scale dryer (Ataç GK 40, Ataç Makina, Turkey) and a laboratory scale steamer (Mathis AG, Switzerland) was used for steam based fixation processes. After printing process, the samples were rinsed at room temperature for 5 minutes, 70 ^{o}C for 10 minutes (three steps) and at room temperature for 5 minutes, respectively.

The reflection (%R) and CIELab values of the samples were measured with a ColorQuest spectrophotometer with a 10° normal observer and norm light D65. The K/S values of the samples were calculated by the Kubelka-Munk equation:

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

where *R* is the reflectance at maximum absorption wavelength (nm), *K* the absorption coefficient and *S* the scattering coefficient.

Table 1. Compositions of pastes for discharge printing

Printing paste	Paste 1	Paste 2	Paste 3
Thickener*	500 g	500 g	500 g
Sodium formaldehyde sulphoxylate	100, 150, 200, 250 g/kg	100, 150, 200, 250 g	-
Zinc formaldehyde sulphoxylate	-	-	40, 70, 100 g/kg
Sodium Hydroxide	-	40 g	-
Sodium Carbonate	-	40 g	-
Water	X	X	X
Total	1 kg	1 kg	1 kg

*Thickener concentration was %10

Table 2. Conditions of fixation methods

Fixation method	Temperature (^{o}C)	Time (min)
Saturated Steam	102	8, 10, 12
Thermofixation	140 150 160 170 180	3, 4, 5, 6
Superheated Steam	140 150 160	2, 4, 6

K/S values of the non-print side of the samples were also measured in order to examine the penetration performances of the pastes.

The bursting strength of the samples was tested by a TMI EC37 Burst Tester.

Three kinds of commercial softeners, whose chemical composition are cationic (soft 1), macro silicone (soft 2) and amino-functional silicone (soft 3) based, respectively, were chosen. The dyed fabric was impregnated with 30 g/l softener liquor at the liquor ratio of 90 % and dried at 100 °C for 5 minutes. After the softening process, discharge printing was applied to the samples. Two kinds of discharge printing types were applied to the samples: 150 g/kg CI RA 2 in neutral conditions and 40 g/kg CI RA 6 (The recipes are given in Table 1). The fixation steps were varied and the face and back sides of the samples were compared in terms of K/S.

In order to investigate the effects of process conditions on the K/S values of the samples statistically, ANOVA test were applied by using SPSS 13.0 for Windows statistical software. To deduce whether the process parameters have significant effects or not, p values were examined. The “p value” that is smaller than 0.05 ($p<0.05$) indicates a significant difference. Table 3 shows the p values obtained from the ANOVA tests.

3. RESULTS AND DISCUSSION

Figure 1 and 2 represents the K/S values of the samples after discharge printing with CI RA 2 and CI RA 6, respectively, with different fixation methods. It is quite clear that the best results were obtained by saturated steam fixation method. On the other hand, superheated steam ensured similar results with saturated steam.

In saturated steam fixation, sodium formaldehyde sulphoxylate gives lower K/S values compared with zinc formaldehyde sulphoxylate even in higher concentrations. Besides, when an alkaline paste is used, the discharging efficiency of the sodium formaldehyde sulphoxylate increases. From the ANOVA analysis, it was found that the effects of the steaming time on the K/S values are statistically insignificant.

Superheated steam fixation leaded to similar results as in saturated steam process in lower fixation times. This seems to be advantageous, however, when Figures 3 and 4 are investigated, it was shown that the penetration of the discharge printing paste to the back side of the sample is unsatisfactory for superheated steam fixation due to the inadequate humidification of the paste. ANOVA analysis showed that the temperature difference in superheated steam fixation is statistically insignificant while the reducing agent concentration is statistically significant. On the other hand, fixation time was found to be statistically significant for CI RA 2, however it was investigated that it is insignificant for CI RA 6.

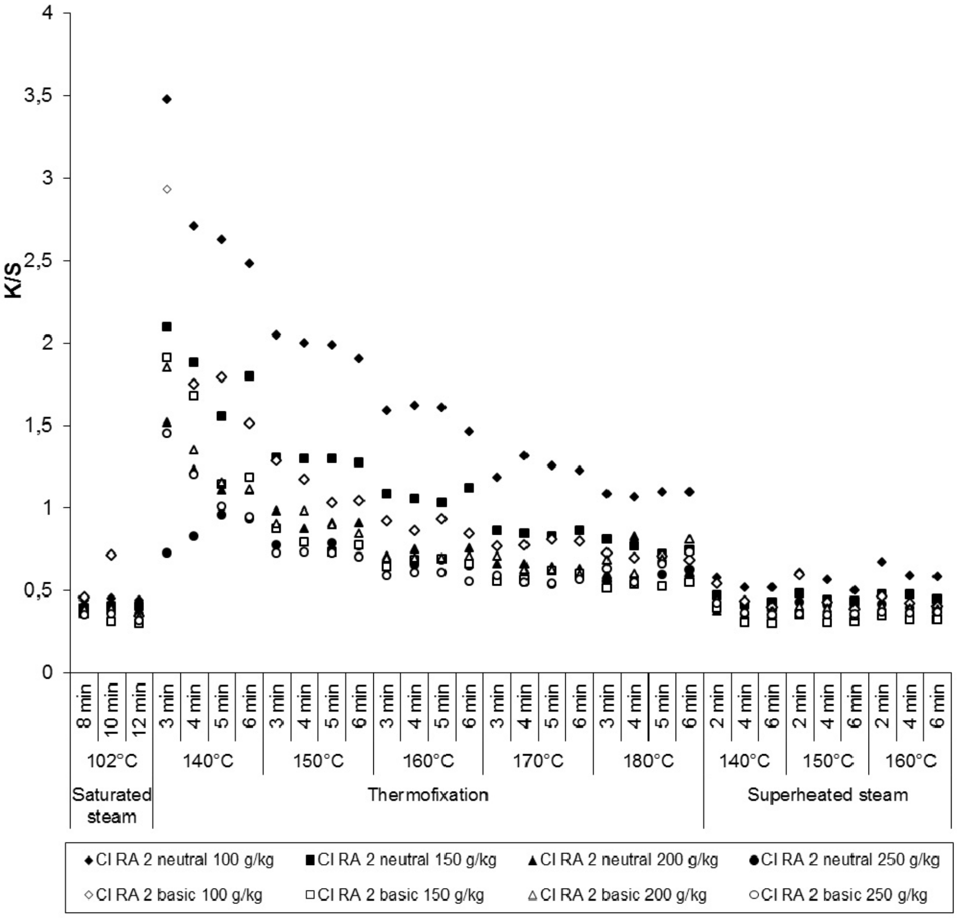

Figure 1. The K/S values of the samples after discharge printing with CI RA 2

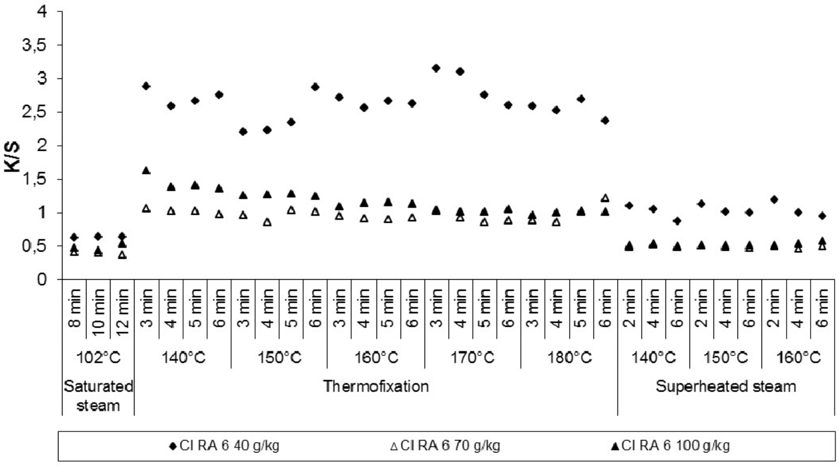

Figure 2. The K/S values of the samples after discharge printing with CI RA 6

Table 3. p values derived from the ANOVA test

	p values		
	CI RA 2 - neutral	CI RA 2 - basic	CI RA 6
Saturated steaming			
Concentration	0.000	0.134	0.116
Time	0.929	0.392	0.926
Thermofixation			
Concentration	0.000	0.000	0.000
Temperature	0.000	0.000	0.421
Time	0.280	0.026	0.934
Superheated steaming			
Concentration	0.000	0.017	0.000
Temperature	0.112	0.565	0.829
Time	0.016	0.004	0.376

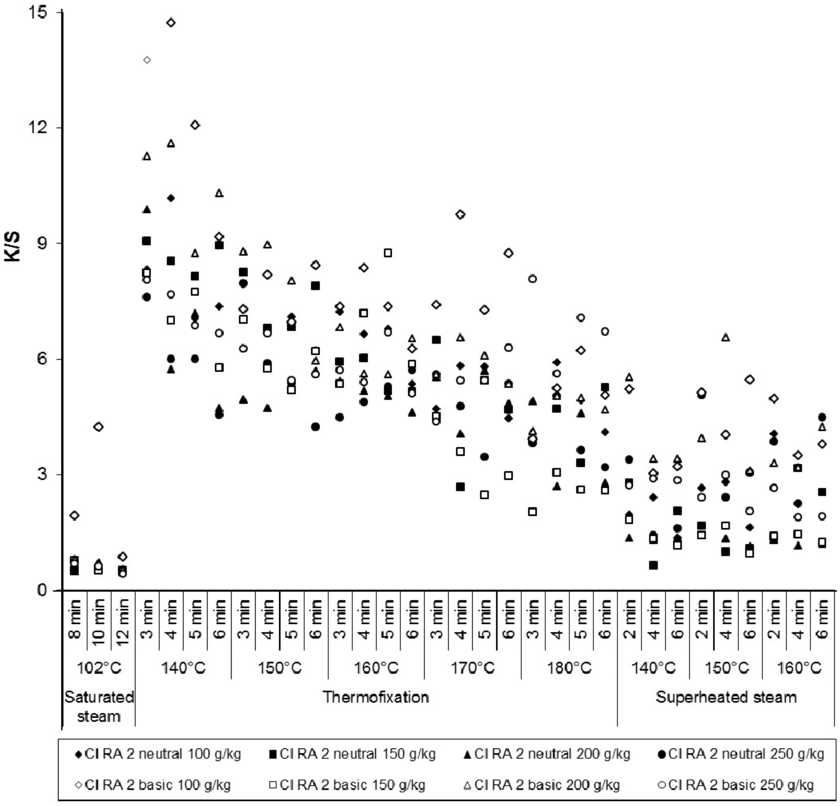

Figure 3. The K/S values of the back sides of the samples after discharge printing with CI RA 2

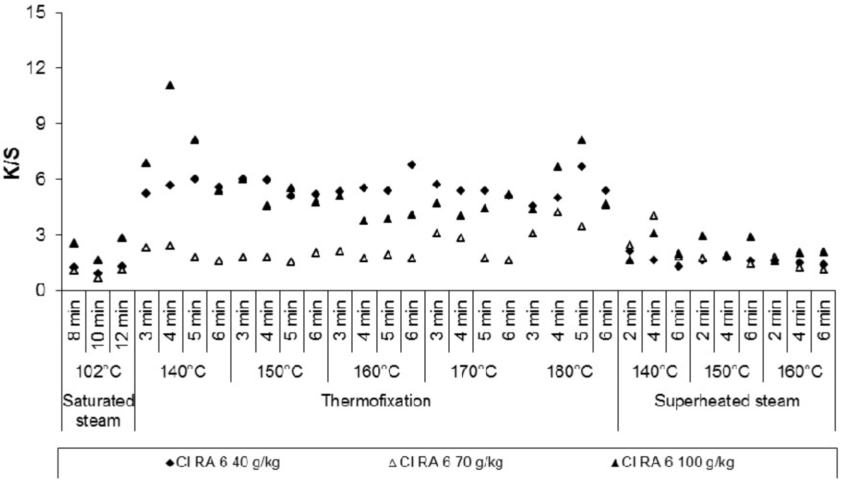

Figure 4. The K/S values of the back sides of the samples after discharge printing with CI RA 6

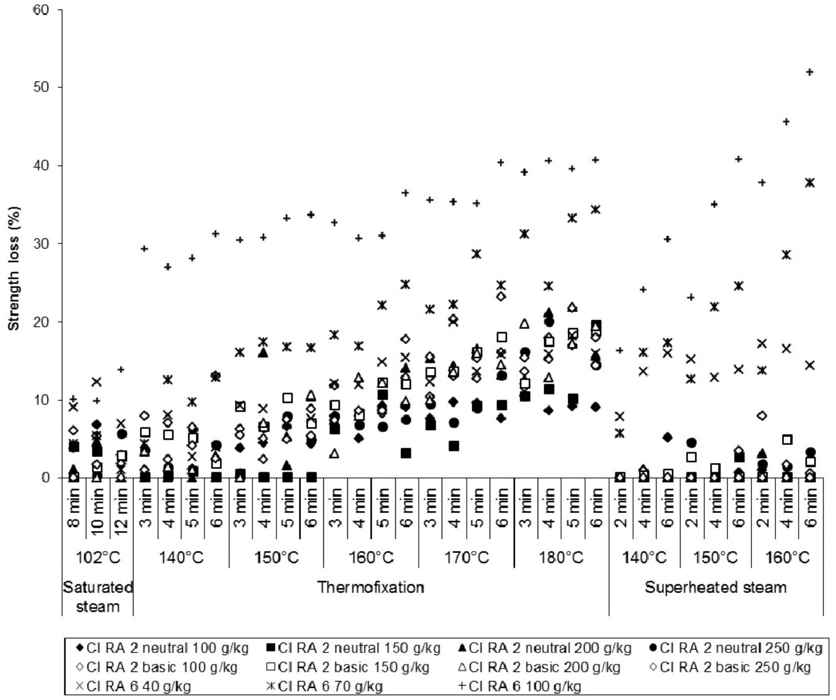

Figure 5. Strength loss after discharge printing

The thermofixation gives the highest K/S values. ANOVA analysis showed that the effects of the thermofixation temperature and the concentration of discharging agent on the K/S values for CI RA 2 are statistically significant. On the other hand, it was observed that the thermofixation temperature is statistically insignificant for CI RA 6 while the reducing agent concentration is statistically insignificant. By the increase in the temperature and discharging agent concentration, the K/S values decreased drastically. However the penetration of the paste to the back side of the samples is the worst compared with other fixation methods, as shown in Figures 3 and 4.

As in saturated steam and superheated steam, sodium formaldehyde sulphoxylate ensured better discharging effects. Additionally, it should be highlighted that the visual investigation of the samples showed that zinc formaldehyde sulphoxylate generally led to uneven discharging effects especially in thermofixation process.

When Figures 3 and 4 were analyzed, it was observed that lowest K/S values of the back faces of the fabrics were obtained by saturated steam fixation for both of the discharging agents. Compared with saturated steam, superheated steam fixation gave higher K/S values for CI RA 2. In thermofixation at 140 °C, 150 °C and 160 °C temperatures, color yield of the back face of the fabrics are higher compared with other methods. By the increase in the temperature (170 °C, 180 °C), K/S values of the back faces decreases. On the other hand, thermofixation of the samples with the use of CI RA 6 with 70 g/kg concentration at 140 °C, 150 °C and 160 °C temperatures led to lower K/S values of the back faces, compared with the use of CI RA 2.

Figure 5 illustrates the strength losses of the samples after discharged printing compared with the untreated sample. In general, sodium formaldehyde sulphoxylate based discharge prints resulted in lower damages compared with zinc formaldehyde sulphoxylate. The discharge printing with CI RA 6 processed in acidic medium. The acetal bonds of the cellulose macromolecules are acid-sensitive, thus the higher strength loss after discharge printing with CI RA 6 compared with CI RA 2 is thought to occurred due to the breaking of the acetal linkages.

For formaldehyde sulphoxylate based discharge printing, saturated steam fixation also resulted in lower strength losses, but the highest bursting strength values were obtained by superheated steam fixation of the samples. This could eventuate due to the lower process times of the superheated steam fixation. On the other hand, due to the lowest penetration of the paste to the back side, there should not be any damage at the back side, thus in total the bursting strength becomes higher. An interesting result is that the superheated steam fixation of the samples includes zinc formaldehyde sulphoxylate exposed to high fiber damage, and by the increase in the concentration, temperature and time, the bursting strength of the samples decreased drastically, and in severe conditions this decrease reached approximately to 50 % of the undischarged sample.

In the thermofixation process, discharge printing with sodium formaldehyde sulphoxylate in neutral conditions clearly gave the lowest strength losses. The temperature of the thermofixation is the main factor that decreases the bursting strength for a given concentration.

Figures 6 and 7 illustrates the color yield values of the softened and discharged printed by CI RA 2 and CI RA 6, respectively. The effects of softeners on the discharging effect by sodium formaldehyde sulphoxylate are not significant. However, when zinc formaldehyde sulphoxylate was used as a discharging agent, it was observed that the K/S of the softened and discharged samples is higher, that means the discoloration efficiency is reduced. The decrease in discharging efficiency is more noticeable after thermofixation. Practically, discharge printing is generally used for piece goods which contain softener, and a thermofixation is applied for the fixation step. Thus the decrease in the discharge efficiency due to the softeners by thermofixation should be marked. This effect is thought to be due to the yellowing tendency of the softeners under high temperature treatments. It is shown from Figure 7 that, especially, the K/S values of the amino-functional silicone based softened (soft 3) samples increases with the increase in the temperature of the thermofixation. The oxidation of the amino groups, which leads to the formation of nitro (-NO_2) groups (10) is thought to be the main factor.

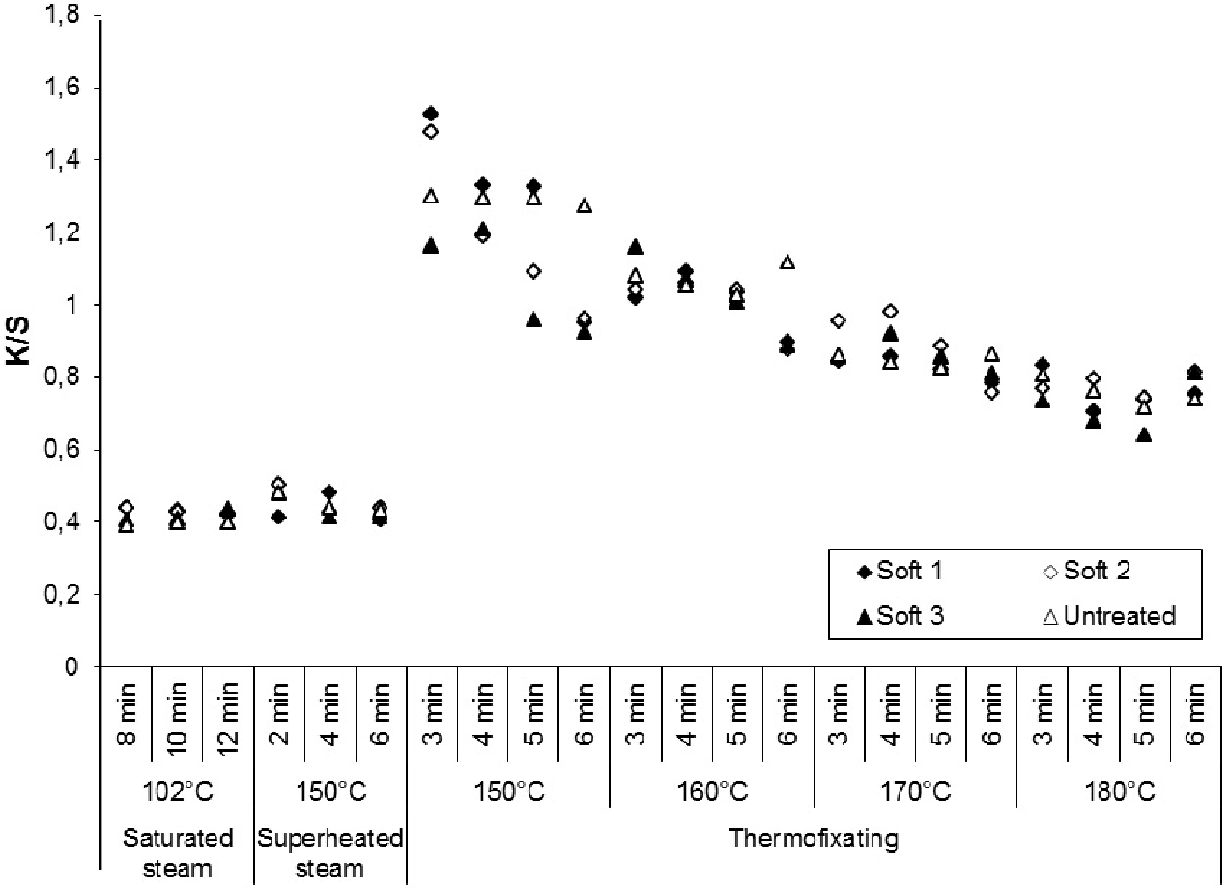

Figure 6. K/S of the samples softened and discharge printed by using CI RA 2

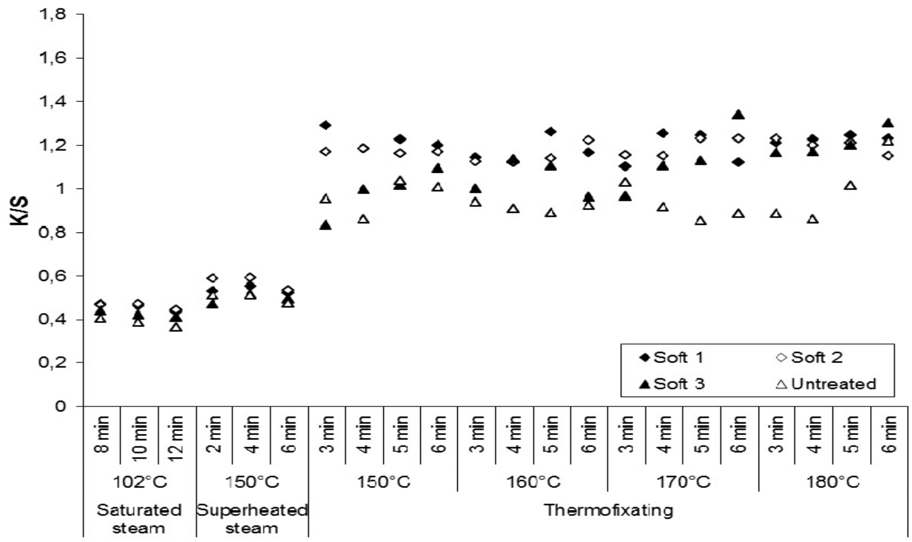

Figure 7. K/S of the samples softened and discharge printed by using CI RA 6

4. CONCLUSIONS

The comparison of the discharging agents and fixation types for discharge printing process were performed in this study. Sodium formaldehyde sulphoxylate gave lower K/S values compared with zinc formaldehyde sulphoxylate. The results for saturated steaming and superheated steaming were found to be similar; however superheated steam leads to an advantage of lower processing times. On the other hand, penetration of the discharge printing paste to the back side of the sample is unsatisfactory for superheated steam fixation due to the inadequate humidification of the paste. Thermofixation gave the higher K/S values, which mean lower discharging efficiency.

Sodium formaldehyde sulphoxylate based discharge prints resulted in lower strength losses compared with zinc formaldehyde sulphoxylate. In general, higher strength values were obtained by saturated steam and superheated steam fixation. However, as an exceptional case, superheated steam fixation of the samples includes zinc formaldehyde sulphoxylate exposed to high fiber damage, and by the increase in the concentration, temperature and time, the bursting strength of the samples decreased drastically. For thermofixation, increase in the temperature and time led to an increase in the strength loss.

It was observed that the effect of the softening is not significant for sodium formaldehyde sulphoxylate discharges; however the existence of the softening agents caused a decrease in discharging efficiency for zinc formaldehyde sulphoxylate discharge printing process.

REFERENCES

1. Dawson T.L. and Hawkyard C.J., 2000, “A new millenium of textile printing”, *Review of Progress in Coloration*, Vol: 30, pp: 7-19.
2. El-Thalouth I.A., Kantouch F., Nassar S.H., El-Hennawi H.M. and Youssef M.A., 2008, “Ecofriendly discharge printing on cotton fabrics using laccase enzyme”, *Indian Journal of Fibre & Textile Research*, Vol: 33, pp: 52-57.
3. Bellini P., Bonetti F., Franzetti E., Rosace G. and Vago S., 2002, *Reference Books of Textile Technologies: Finishing*, Italian Association of Textile Machinery Producers (ACIMIT), Milan, 3rd Edition.
4. Glover B., 2005, “Reactive dyes for textile printing”, *Colourage*, Vol: 52, pp: 67-81.
5. Berry C. and Ferguson J.G., 1994, “Discharge, Resist and Special Styles” (Chapter 6) in, Miles LWC, *Textile Printing*, Society of Dyers and Colourists, England, 2nd Edition.
6. Lewis D.M., 1992, *Wool Dyeing*, Society of Dyers and Colourists, England, pp: 345-346.
7. Rouette H.K., 1995, *Lexikon für Textilveredlung*, Laugmann-Verlag, Dülmen, Germany.
8. Tomasino C., 1992, *Chemistry & Technology of Fabric Preparation & Finishing*, NCSU Raleigh, North Carolina, USA, pp: 134-153.
9. Özgüney A.T. and Özkaya K., 2008, “Effects of the softeners on the colour change which occurs during the curing of cotton fabric in screen printing conditions”, *Tekstil ve Konfeksiyon*, Vol: 18(2), pp: 121-129.
10. Gokulnathan S. and Thomas P.T., 2005, “Organomodification of Silicones for Textile Applications”, *Colourage*, Vol: 2, pp: 47-50.