(REFEREED RESEARCH)

ZINC CHLORIDE TREATED AND SILICONE SOFTENED COTTON FABRIC: EFFECT OF WASHING ON ANTIBACTERIAL PROPERTIES

ÇİNKO KLORÜR İŞLEMLİ VE SİLİKONLA YUMUŞATILMIŞ PAMUKLU KUMAŞ: YIKAMANIN ANTİBAKTERİYEL ÖZELLİĞE ETKİSİ

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ABSTRACT

Cotton fabrics were treated with zinc chloride under different conditions to develop antibacterial properties. The treated and untreated cotton fabric samples were dyed with reactive dye and silicone softened by the exhaustion technique. The treated fabrics were washed 10 times to determine the retention of antibacterial properties. The selected dyed cotton fiber sample surfaces were observed by a scanning electron microscope. The experimental results of the study showed that antibacterial properties could be obtained by treatment with zinc chloride on cotton fabrics. In addition, after repeated washing of the treated cotton fabrics 10 times, the antibacterial efficiency of the related fabrics was observed at different levels. The dyeing properties of zinc chloride treated cotton fabrics will be determined in another study.

Key Words: Cotton, Zinc chloride, Antibacterial fabric, Silicone softening.

ÖZET

Pamuklu kumaş çinko klorür ile farklı şartlarda antibakteriyel kumaş elde etmek için işlem yapılmıştır. İşlemli ve işlemsiz kumaş örnekleri çektirme yöntemine göre reaktif boya ile boyanmış ve silikonla yumuşatma işlemi yapılmıştır. İşlemli kumaş örnekleri antibakteriyel özelliğin kalıcılığının belirlenmesi için 10 kez yıkanmıştır. Seçilen boyalı lif örnekleri yüzeyi elektron mikroskobu ile gözlemlenmiştir. Deneysel çalışma sonuçları pamuklu kumaşa çinko klorür ile işlemi ile antibakteriyel kumaş elde edilebileceğini göstermiştir. Ek olarak, 10 kez yıkama sonucunda farklı seviyelerde antibakteriyel etki gözlemlenmiştir. Çinko klorür ile işlemli kumaşa ait boyanma özellikleri bir başka çalışmada belirlenecektir.

Anahtar Kelimeler: Pamuk, Çinko klorür, Antibakteriyel kumaş, Silikonlu yumuşatma.

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1. INTRODUCTION

Cotton is a natural vegetable fiber and exhibits soft, smooth and breathable textile surfaces. Reactive dyes are widely used in the dyeing of cotton fibers. They react with the fiber in aqueous alkali medium and form covalent bonds with the fiber (1-2). Textile materials produced from cotton fiber are known to be susceptible to microbial attack, as the fibers provide a large surface area and absorb moisture, thus generating a suitable environment for microbial growth and multiplication. This often leads to an objectionable odor, dermal infection, product deterioration, allergic responses and other related problems. Several types of antimicrobial agents, such as chitosan, quaternary ammonium compounds, silver and zinc related metallic compounds are used in textile materials to confer antimicrobial properties (3-7). In the literature, there are various studies about zinc related cotton fabric treatment. Iamphaojeen *et al*. developed an antibacterial cotton fabric which involved immobilization of ZnO nanoparticles using poly 4-styrenesulfonic acid (8). Selvam *et al*. functionalized cotton fabric with poly-N-vinyl-2-pyrrolidone and padded ZnO nanoparticles. Their treated cotton fabric showed very good antibacterial activity (9). Gowri *et al*. developed a new class of nanofinishing materials with ZnO nanoparticles and poly(methylmethacrylate) for the protection of polyamide fabrics against UV radiation (10). Gronsek *et al*. studied the effect on dyeability, with monobifunctional reactive dyes, of a cotton fabric treated under different conditions of zinc chloride using an all-in jet dyeing process. Their results showed that the degree of dye fixation to the substrate can be increased by pretreatment in a zinc chloride solution (11). Mostashari *et al*. applied a phosphorus-zinc chloride combination to cotton fabric, they stated that cotton treated with this combination was effective for flame-retardancy (12). Mary *et al*. studied the biocidal action of zinc loaded grafted cotton fabric. Their study indicated that the growth rates of bacterial colonies were appreciably low in the presence of Zn loaded grafted fibers (13). The aim of this present work was to determine easy and simple conditions for the application of zinc chloride to cotton dyeing to obtain antibacterial fabrics (14).

2. EXPERIMENTAL

2.1. Fabrics

The cotton fabric ready for dyeing was supplied by Balgünes Textile Company (Kayseri, Turkey). The characteristics of the fabric were plain, knitted and with weight of 145 g/m^2. The fabrics were washed with a solution of nonionic detergent (1 g/l) for 30 min at 50 ^oC, thoroughly rinsed, and dried at room temperature.

2.2. Chemicals and dye

Zinc chloride, soda and Glauber's salt were used at commercial grade. Solusoft Acn liq (Clariant, Turkey) silicone softening agent was used for softening the cotton. The Drimaren Blue CL-BR (CI Reactive Blue 19) commercial reactive dye was used in this study (15).

2.3. Fabric zinc chloride treatment, dyeing and softening

The cotton fabric samples were treated with zinc chloride in three different methods. About 5 g of fabric was weighted and liquor to fabric ratio of 20:1 was used.

T1: Pre-treatment process began at 25 ^oC in the baths containing 1, 2, 3% owf (on weight for fabric) zinc chloride. The temperature was then raised to 70 ^oC in 45 min and held constant for 30 min. After pre-treatment, dyeing process began at 25 ^oC in the dye-baths containing 50 g/l Glauber's salt, 20 g/l soda and 1% dye. The temperature was then raised to 70 ^oC in 45 min and held constant for 45 min. The temperature was decreased to 25 ºC, the fabric samples were softened with silicone softening agents (3% owf) and rinsed by cold tap water, washed at the boiling temperature, rinsed by cold tap water and then dried under the laboratory conditions.

T2: Combined treatment began at 25 ^oC in the dye-baths containing: 50 g/l Glauber's salt, 20 g/l soda, 1% dye and 1, 2 and 3% owf zinc chloride. The temperature was then raised to 70 ^oC in 45 min and held constant 45 min. The temperature was decreased to 25 ºC, the samples were softened by silicone softening agents (3% owf) and rinsed by cold tap water, washed at the boiling temperature, rinsed by cold tap water and then dried under the laboratory conditions.

T3: Post-treatment began at 25 ^oC in the dye-baths containing: 50 g/l Glauber's salt, 20 g/l soda and 1% dye. The temperature was then raised to 70 ^oC in 45 min and held constant for 45 min. The temperature was decreased to 25 ºC, the samples were rinsed by cold tap water, washed at boiling temperature and rinsed by cold tap water. The fabric samples were softened by silicone softening agents and then dried under the laboratory conditions. The used treatment types of the cotton fabrics are shown in Figure 1.

2.4. Repeated washing

To evaluate the durability of the zinc chloride application against repeated washing, samples were washed 10 times in soft water at a 1/20 liquor ratio, at 40 ^oC for 10 min. Ece detergent (1 g/l) was added only at the 5th wash. The washed fabric samples were dried at ambient temperature.

2.5. Test bacteria and antimicrobial test

Cultures of the following two different bacteria were used in the study: *Escherichia coli* (ATCC 11229), *Staphylococcus aureus* (ATCC 25923). Before the antimicrobial tests, all bacteria from the fresh culture were grown in nutrient broth at 37 ^{o}C for 18 h.

In the first set of experiments the agar diffusion test method was used for the aqueous sterilized zinc chloride solutions of three different (1%, 2% and 3%) concentration levels. A nutrient agar medium (g/l: peptone 5.0; beef extract 1.5; yeast extract 1.5; NaCl 5.0; agar 20; pH 7.5) was prepared and autoclaved at 121 ^oC for 15 min. Sixty microliters of zinc chloride solution was poured into wells on nutrient agar. Petri plates were incubated at 37 ^oC for 24 h. At the end of this period, the zone of inhibition (ZOI) which formed on the medium was measured in millimeters (mm) (16-17).

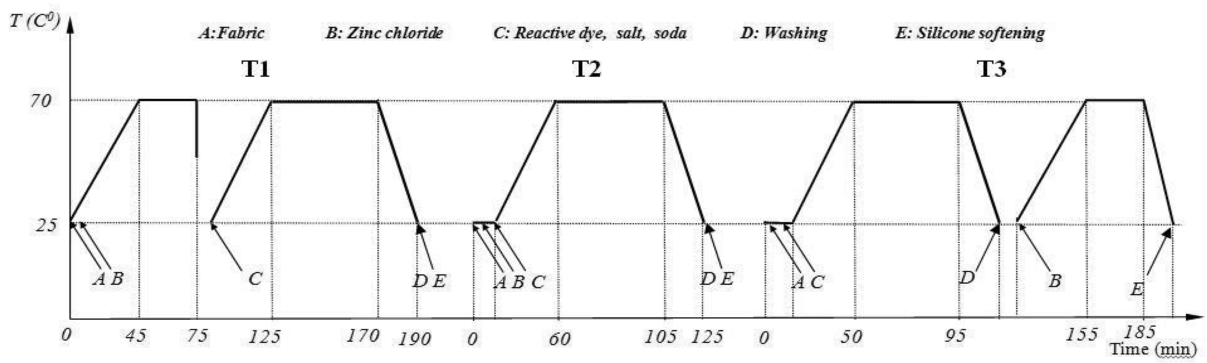

Figure1. Zinc chloride treatment type and reactive dyeing

The ASTM E2149-1 test method was used to determine the bacteriodynamic activity (inhibition of multiplication) as well as the bactericidal activity (killing of bacteria) of the dyed cotton fabrics against selected bacterial species. A 0.5 g sample of sterile fabric (treated and untreated) was introduced into the 10 ml buffered solution with the desired microbe and incubated at 37^{o}C. At 0 and 2 h, the number of colonies in the tubes was counted using the serial dilution method on nutrient agar. The reduction percent caused by each concentration of the zinc treated and untreated samples on test bacteria were expressed as follows:

$$R_1 = \frac{C_0 - C_f}{C} \times 100\ (\%) \quad (2)$$

$$R_2 = \frac{C_{f\,0} - C_f}{C_f} \times 100\ (\%) \quad (3)$$

where C_0 (cfu) is the number of microbial colonies on the control fabric at 0 hours (untreated fabric), $C_{f\,0}$ (cfu) is the number of microbial colonies on the zinc treated fabric at 0 hours. C_f (cfu) is the number of microbial colonies on the zinc treated fabric after 2 hours. R_1 (%) is the reduction in bacterial population according to control fabric and R_2 (%) is the reduction in bacterial population according to itself.

2.6. Scanning electron microscope (SEM) analysis

A LEO 440 scanning electron microscope (SEM) was used to analyze the surface morphology of the zinc treated cotton fibers. The samples were prepared by the standard preparative technique of applying a gold layer to produce a conductive surface (18).

3. RESULTS AND DISCUSSION

3.1. Antimicrobial activity of zinc chloride solutions

Three different concentrations of zinc chloride were screened for their antimicrobial activity against selected microbes (*E. coli,* and *S. aureus*). Examples of a clear ZOI by zinc chloride against selected microbes can be seen in Figures 2.

The effect of zinc chloride concentrations on antimicrobial activity was studied further and the results are summarized in Table 1. A zone of inhibition (diameter, mm) was determined in each case. It was observed that an increase in zinc chloride concentration led to an increased ZOI as can be seen by the enhancement in the zone diameter.

Table 1. Zone of inhibition for zinc chloride solution against selected microbes

Zinc chloride conc. (%)	Zone of inhibition (diameter, mm)	
	E. coli	*S. aureus*
0	0	0
1	8	8
2	9	9
3	12	13

3.2. Antibacterial activity of zinc treated fabrics

The percentage of microbial reduction in the cotton fabrics treated with zinc chloride at three different concentration levels (1%, 2%, and 3%) against selected bacteria are given in Table 2 and Table 3, respectively.

In Table-2, the highest antibacterial level against *E.coli* is obtained in T3 treatment type; however in general, the least antibacterial efficiency is obtained in T1 in each of the zinc chloride application percentages. The washing treatment decreased antibacterial efficiency. However, there is an irregular increase in the R1% and R2% as seen for T3-3. In general, the antibacterial efficiency varies between 19.4%-87.9% in the three types of treatments by applying zinc chloride in different percentages.

In Table-3, the highest antibacterial level against *S.aureus* is obtained in the T3 treatment type; however in general, the least antibacterial efficiency is obtained in T1 in each of the zinc chloride application percentages. However the efficiency levels in different types of treatments are close to each other compared to Table-2. There is an irregular increase in the R1% and R2% as seen in T1-2 and T2-3. In general, the antibacterial efficiency varies between 50%-93.7% in three types of treatments by applying zinc chloride in different percentages.

3.3. Surface morphology

The SEM images (Figure 3, a-c) show no distinguishable physical modification of the cotton fiber surface. The surface of the treated cotton fiber is smooth and undamaged. There are mineral deposits on the surface of the cotton fiber (3a and 3c).

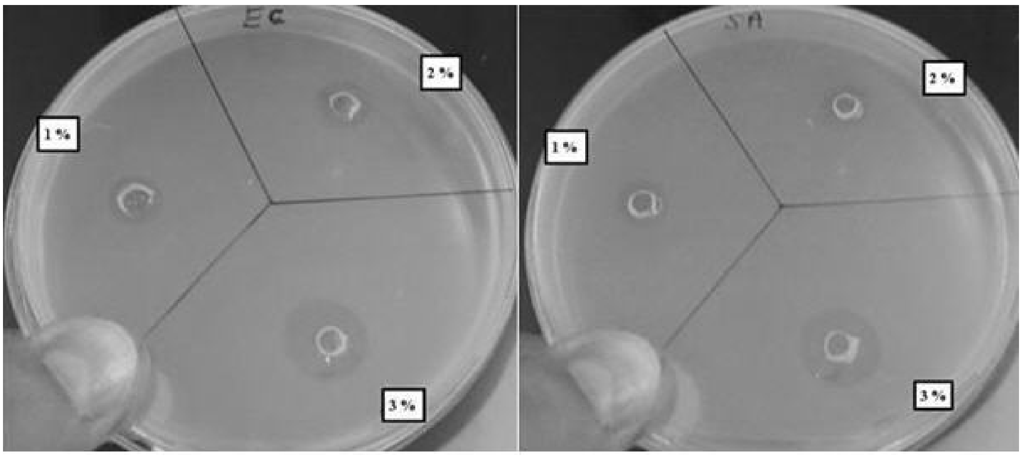

Figure 2. Antimicrobial activity of the zinc chloride solutions against *E.coli* (EC) and *S.aureus* (SA).

Table 2. Antibacterial activities of treated fabrics against *E.coli*

Fabric treatment type	Zinc chloride concentration, (owf)	Dyed and silicone softened fabric samples				10 times repeated washed fabric samples			
		Surviving cells cfu/ml		Bacterial reduction, %		Surviving cells cfu/ml		Bacterial reduction, %	
		at zero time	after two hours	R1	R2	at zero time	after two hours	R1	R2
Untreated	0	$2.33*10^{7}$	$4.16*10^{7}$	multiplication		$1.33*10^{7}$	$2.83*10^{7}$	multiplication	
T1	1	$1.66*10^{7}$	$1*10^{7}$	40	75.9	$1.5*10^{7}$	$8.33*10^{6}$	44	19.4
	2	$2.66*10^{7}$	$1.33*10^{7}$	50	68	$2.16*10^{7}$	$1.08*10^{7}$	50	61.7
	3	$1.66*10^{7}$	$9.16*10^{6}$	45	78	$2*10^{7}$	$6.66*10^{6}$	66.6	76.4
T2	1	$3.16*10^{7}$	$1.78*10^{7}$	43,6	57.2	$2.66*10^{7}$	$1.66*10^{7}$	37.5	41.1
	2	$2.83*10^{7}$	$1*10^{7}$	64,7	75.9	$1.66*10^{7}$	$9.66*10^{6}$	42	65.8
	3	$3.33*10^{7}$	$8.33*10^{6}$	75	80	$1.83*10^{7}$	$8.24*10^{6}$	55	70.8
T3	1	$2.33*10^{7}$	$1.33*10^{7}$	42,8	68	$2.33*10^{7}$	$1.02*10^{7}$	56	63.7
	2	$2.83*10^{7}$	$1.07*10^{7}$	62	74.1	$2.66*10^{7}$	$8.33*10^{6}$	68.7	70.5
	3	$3.83*10^{7}$	$5. *10^{6}$	86,9	87.9	$2.5*10^{7}$	$1.33*10^{7}$	46.6	52.9

Table 3. Antibacterial activities of treated cotton fabrics against *S.aureus*

Fabric treatment type	Zinc chloride concentration, (owf)	Dyed and silicone softened fabric samples				10 times repeated washed fabric samples			
		Surviving cells cfu/ml		Bacterial reduction, %		Surviving cells cfu/ml		Bacterial reduction, %	
		at zero time	after two hours	R1	R2	at zero time	after two hours	R1	R2
Untreated	0	$2.16*10^{7}$	$3.99*10^{7}$	multiplication		$2.83*10^{7}$	$4.16*10^{7}$	multiplication	
T1	1	$1.58*10^{7}$	$6.99*10^{6}$	55.8	82.5	$1.5*10^{7}$	$6.99*10^{6}$	53.3	83.2
	2	$1.99*10^{7}$	$7.83*10^{6}$	60.8	80.4	$2.33*10^{7}$	$9.49*10^{6}$	59.3	77.2
	3	$1.83*10^{7}$	$7.99*10^{6}$	56.3	80	$2.33*10^{7}$	$6.66*10^{6}$	71.4	84
T2	1	$1.83*10^{7}$	$4.83*10^{6}$	73.6	87.9	$2*10^{7}$	$6.49*10^{6}$	67.5	84.4
	2	$1.66*10^{7}$	$5.16*10^{6}$	69	87	$1.66*10^{7}$	$3.33*10^{6}$	80	92
	3	$2*10^{7}$	$4.99*10^{6}$	75	87.5	$2.83*10^{7}$	$6.66*10^{6}$	76.4	84
T3	1	$2.16*10^{7}$	$7.33*10^{6}$	66.1	81.6	$1.83*10^{7}$	$4.83*10^{6}$	73.6	88.4
	2	$2.33*10^{7}$	$1.16*10^{7}$	50	70.8	$1.66*10^{7}$	$4.83*10^{6}$	71	88.4
	3	$2*10^{7}$	$2.49*10^{6}$	87.5	93.7	$3*10^{7}$	$4.66*10^{6}$	84.4	88.8

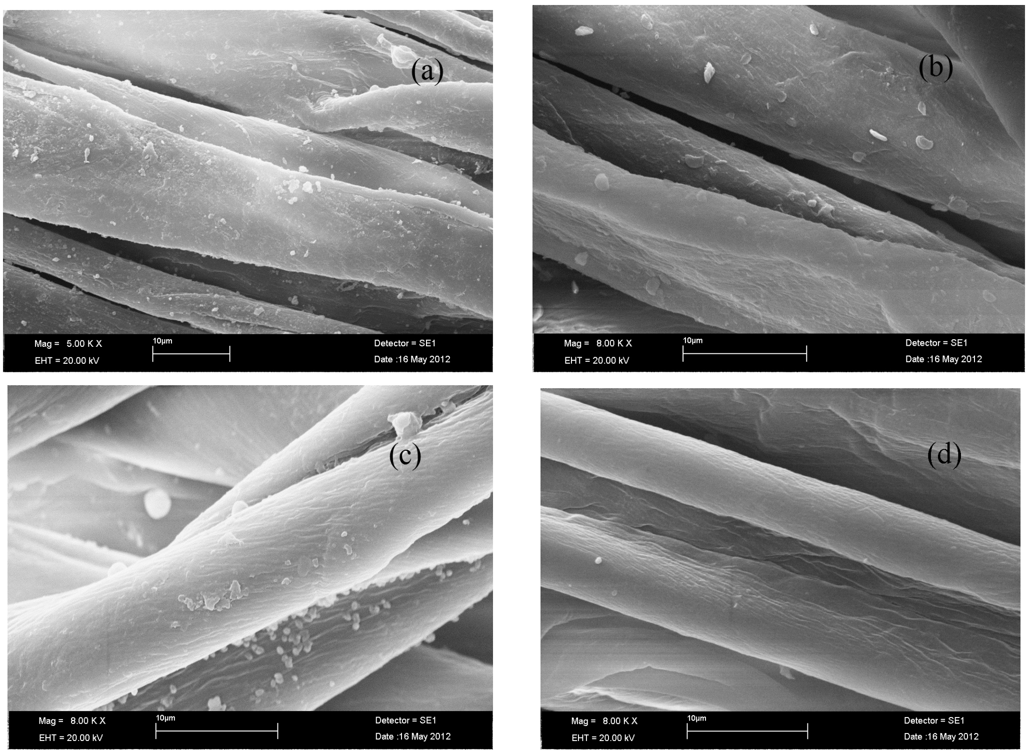

Figure 3. Selected SEM images at various magnification of zinc treated and untreated cotton fabrics. (a) T1 treated; (b) T2 treated; (c) T3 treated and (d) untreated.

4. CONCLUSION

As a result of this experimental study, the antibacterial properties of zinc chloride treated cotton fabrics were investigated according to evaluation of ASTM E2149-1 bacteriodynamic antibacterial standard. Zinc chloride was applied to the cotton fabrics in three different concentrations by using the pre-treatment, combined, and post-treatment exhaustion techniques. In order to determine antibacterial durability to home laundering, 10 times repeated washing of the treated cotton fabrics was performed. The antibacterial properties of the zinc chloride treated cotton fabrics against *E.coli* and *S.aureus* pathogenic bacteria were obtained at different levels. The repeated washing treatment decreased antibacterial efficiency. For all zinc application methods, the T3 treatment type was found to be better than T1 and T2 in terms of the fabric antibacterial properties.

Given the other studies in literature, it is found that the application method in this study is better than the other methods mentioned in the literature survey in terms of easy application and combinable to dyeing. On the other hand, according to the experimental results, it was found that zinc chloride treatment can be used in cotton finishing for easy antibacterial functioning.

REFERENCES

1. Broadbent, A.D., 2001, "Reactive Dyes", *Basic Principles of Textile Coloration*, SDC Publication, West Yorkshire, s:332-357.
2. Demir, A., Öktem, T., Seventekin, N., 2008, "The Effect of UV-Absorbers on Light Fastness of Reactive Dyed Cotton Fabrics", *Tekstil ve Konfeksiyon*. 18(3), s:211-220.
3. Sivakumar, A., Murugan, R., Sundaresan, K., 2013, "Certain investigations on the effect of nano metal oxide finishes on the multifunctional characteristics of cotton fabrics", *Journal of Industrial Textiles*, 43(2), s:155-173.
4. Ursache, M., Loghin, C., Muresan, R., Cerempei, A., Muresan, A., 2011, "Investigation on the Effects of Antibacterial Finishes on Dyed Cotton Knitted Fabrics", *Tekstil ve Konfeksiyon*, 21(3), s:249-256.
5. Klemencic, D., Tomsic, B., Kovac, F., Simoncic, B., 2012, "Antimicrobial cotton fibres prepared by in situ synthesis of AgCl into a silica matrix", *Cellulose,* 19(5), s:1715-1729.
6. Teli, M.D., Sheikh, J., 2012, "Antibacterial and Acid and Cationic Dyeable Bamboo Cellulose (Rayon) Fabric on Grafting", *Carbohydrate Polymers*, 88(4), s:1281-1287.
7. Yıldırım, O., Sevim, A., Gul, A., 2012, "Novel Water-Soluble Metallophthalocyanines Supported on Cotton Fabric", *Coloration Technology*, 128(3), s:236-243.
8. Iamphaojeen, Y., Shriphannon, P., 2012, "Immobilization of Zinc Oxide Nanoparticles on Cotton Fabrics Using Poly 4-stryrenesulfonic Acid Polyelectrolyte" *International Journal of Materials Research*, 103(5), s:643-647.
9. Selvam, S., Sundrarajan, M., 2012, "Functionalization of Cotton Fabric with PVP/Zno Nanoparticles for Improved Reactive Dyeability and Antibacterial Activity" *Carbohydrate Polymers*, 87(2), s:1419-1424.
10. Gowri, V.S., Almeida, L., De Amorim, M.T.P., Pacheco, N.C., Souto, A.P., Esteves, M.F., Sanghi, S.K., 2011, "Functional Finishing of Polyamide Fabrics Using ZnO-PMMA Nanocomposites", *Journal of Materials Science*, 45(9), s:2427-2435
11. Gronsek, M., Recelj, P., Bukosek, V., 2001, "Effect of Zinc Chloride on the Dyeability of cotton with bis(monofluoro-s-triazine) dye", *Textile Research Journal*, 71(4), s:351-356.
12. Mostashari, S.M., Fayyaz, F., 2008, "A Combination of Red Phosphorus-Zinc Chloride for Flame-Retardancy of a Cotton Fabric", *International Journal of Polymeric Materials*, 57(2), s:125-131.
13. Mary, G, Bajpai, S.K., Chand, N., 2010, "Antibacterial Activity of Zn-Loaded Grafted Fibers-Mechanical Strength and Biocidal Action", *Journal of Natural Fibres*, 7(1), s:34-41.
14. Sıdar, B., 2013, "Determination of Antibacterial Properties and Dyeing of Cotton Fabrics Treated with Zinc Salt", M.Sc. Dissertation, University of Erciyes, Kayseri/Turkey.
15. http://www.lookchem.com/cas-258/2580-78-1.html (Last accessed: January, 2014).
16. Tutak, M., Gun, F., 2011, "Antimicrobial Effect Of C.I. Basic Red 18:1 And C.I. Basic Yellow 51 On Some Pathogenic Bacteria", *Fibres and Polymers*, 12(4), s:457-460.
17. Tutak, M., Gun, F., 2012, "Antimicrobial Effect of CI Basic Green 4 (Malachite Green) Against Some Pathogenic Bacteria", *Tekstil ve Konfeksiyon*. 22(1), s:48-51.
18. Tutak. M., Özdemir, F., 2011, "Fastness And Dyeability Improvement Of Wool Fabric Pretreated With Oxalate Derivatives", *Journal of Applied Polymer Science,* 2011, 122(5), s:3440-3445