(REFEREED RESEARCH)

SHADING OF POLYAMIDE 6.6 AFTER MULTI WASHING PROCESS AND INVESTIGATION OF CHEMICAL CHANGES ON FABRIC SURFACE

TEKRARLI YIKAMA İŞLEMLERİ SONRASI POLİAMİD 6.6'NIN NÜANSLANMASI VE KUMAŞ YÜZEYİNDE KİMYASAL DEĞİŞİMLERİN İNCELENMESİ

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ABSTRACT

When white fabrics are subjected to repeated washing process with home type laundry detergent, whiteness is decreased and yellowing or graying become evident. Post-wash protection of fabric whiteness is provided with various additives such as fluorescent whitening agent, shading dyes in detergent contents. The aim of this research is to investigate the usage of shading dyes for preventing the complaints of graying/yellowing occurring after multi washing process in polyamide fabrics. Chemical effects over the multiwashed polyamide fabrics were explained by using standard test methods. The whiteness index of fabrics (WI CIE) was measured by spectrophotometer. Post-multiple washing effects were evaluated by loss of strength, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). According to the results, detergent formulation including Disperse Violet 28® shading dye showed better whiteness index in spite of having 10% bleaching system than detergent formulation including Direct Violet 9® shading dye having 12% bleaching system. Statistical evaluation of bursting strength showed that the same strength losses on fabrics in both detergent formulas occurred. Calcium carbonate was determined on polyamide fabric surface by FTIR and XPS results supported this finding.

Keywords: Detergent, Shading Dye, Direct Violet 9, Disperse Violet 28, Whiteness Index, Polyamide.

ÖZET

Beyaz kumaşlar ev tipi çamaşır deterjanları ile tekrarlanan yıkama işlemine tabi tutulduğunda beyazlık azalmakta, sararma veya grileşme belirginleşmektedir. Kumaş beyazlığının yıkamadan sonra korunması, deterjan içeriğindeki floresan beyazlatma maddesi, nüanslama boyası gibi çeşitli katkı maddeleriyle sağlanmaktadır. Bu çalışmanın amacı, poliamid kumaşlarda çoklu yıkama işleminden sonra oluşan grileşme / sararma şikayetlerini önlemek için nüanslama boyalarının kullanımını araştırmaktır. Tekrarlı yıkanan poliamid kumaşlar üzerindeki kimyasal etkiler standart test yöntemleri kullanılarak açıklanmaktadır. Kumaşların beyazlık indeksi (WI CIE) spektrofotometre ile ölçülmüştür. Tekrarlı yıkama işleminin etkisi, mukavemet kaybı, taramalı elektron mikroskobu (SEM), X-ışını fotoelektron spektroskopisi (XPS) ve Fourier transform infrared spektroskopisi (FTIR) ile değerlendirilmiştir. Sonuçlara göre, % 10 beyazlatma sistemine sahip Disperse Violet 28® nüanslama boyası içeren deterjan formülasyonu,% 12 beyazlatma sistemine sahip Direct Violet 9® nüanslama boyası içeren deterjan formülasyonuna göre daha iyi beyazlık indeksi göstermektedir. Patlama mukavemetinin istatistiksel değerlendirilmesi, her iki deterjan formülünde de kumaşlarda aynı miktarda güç kaybının meydana geldiğini göstermektedir. Poliamid kumaş yüzeyi üzerinde kalsiyum karbonat olduğu FTIR ile belirlenmiştir ve XPS sonuçları da bu bulguyu desteklemiştir.

Anahtar Kelimeler: Deterjan, Nüanslama Boyası, Direkt Viyole 9, Dispers Viyole 28, Beyazlık İndeksi, Poliamid.

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INTRODUCTION

As time passes and the duration of use increases, white textiles tend to lose their first day's appearances, they turn into a grayish, yellowish or pale tint. The optical whiteners on the white textile material which were applied during textile finishing decrease and especially after repeated washing this decrease become more evident. Detergent producers try to overcome this problem by adding many ingredients to detergent formulations.

Yellowing of a fabric after washing is explained by oxidation and polymerization of certain fractions of body oils that have not been removed during washing. Some other factors also affect the yellowing of textiles such as fiber degradation, various additives, excess alkalinity, bleaching effects, hard water soaps and residual laundry chemicals [1].

White fabrics are subjected to repeated washing process with home type laundry detergent throughout lifetime and post-wash protection of fabric whiteness is tried to be provided with various additives (such as fluorescent whitening agent, shading dyes) in detergent contents.

To obtain fabric whiteness, the surface of the fabric must be thoroughly cleaned [2,3]. For this purpose, the white fabrics should be washed with a detergent composition containing bleaching system. The bleaching system used in home type laundry detergent is a complex system in which many materials are used together. This system consists of materials such as bleaching particles (such as percarbonate, perborate, hypocloride), bleaching catalyst, pre-formed peracids, bleach activator (such as tetraacetyl ethylene diamine (TAED), sodium nona noyloxy benzenesul fonate (NOBS)), photo bleachers, bleaching enzymes and any combination thereof [4]. Bleaching is a chemical process which may have negative effects over the fabrics' strength in long term and also dominant role in pushing up the production costs.

Increasing the emission of light from the surface by using of fluorescent whitening agents (FWAs) may be used for fabric whiteness. The FWAs are aromatic compounds that deposit on the fabric. They absorb UV light and emit visible light, thereby increasing the emission from the fabric surface, making it appear whiter/brighter [2].

Another way to achieve whiteness is altering the hue of the fabric by tinting. For this purpose, shading dyes are used. They are substantive colorants and added to the detergents at low levels. Generally blue and violet colors are used as shading dyes. The shading material should deposit evenly on the fabric and it works by altering the shade of the fabric [2]. Shading dyes added in detergent formulation, first dissolve into the wash solution and then deposit onto the fabrics giving a pleasing white shade to textile materials [5]. The purpose of shading dyes is typically to counteract the fading and yellowing of the textile substrates by providing a purple or blue hue to the laundered fabrics, reducing the visual impact of the yellowing. Generally, shading dyes are effective for shading a specific textile type, either cotton or synthetic fabrics because of their chemical composition. However, the fabric after repeated laundry usually shows a purple or blue hue, indicating that too much hueing dyes may have undesirably deposited on the fabric surface [6].

The color yellow is produced by partial absorption of the long wavelength band of sunlight, and leads to a deficiency of reflected blue light. Hueing dye can make garments appear white by shading the undesired yellow color and making it less noticeable. It can also improve the whiteness by addition of a complementary color to the fabric. As a result, hueing dye provides fabric with a soft luster as a result of the blocking of the yellowish tinge [7].

There are some classifications of shading dyes. One way is to classify the dyes depends on their structures such as azo dyes and anthraquinone dyes. Another way is to classify them according to their mode of application such as direct, acid, disperse, vat, and solvent dyes. According to another method of classification, dyes are called hydrophobic or hydrophilic depending on their affinity to the fabrics. Another way of classifying shading dyes depends on whether the dyes deposit onto fabrics after a single-wash to show their effect, or whether they deposit after multiple washes. Dyes that deposit in a single-wash are called one-wash dyes. The others are called build-up dyes [8].

In the study of Batchelor et al., detergent formulations consisting of Acid Violet 50, Direct Violet 9, Disperse Violet 28 and cationic phenazine dye were prepared. In the same washing cycle, it was attempted to find a dye combination which gives good build-up on the cotton-polyester fabric without excessive accumulation on the cotton fabric [9].

A mixture of cotton, polyester-cotton, polyester, polyamide-elastane and cotton-elastane fabrics were washed with a formulation containing 0.005 wt % of Disperse Violet 28 and a control without dye [10]. According to results, the Disperse Violet 28 shading dye was deposited on all tested fiber types in the same wash.

In the research of Pei and et al. the deposition mechanism of shading dyes on different fabric surfaces was studied. The accumulation level of shading dyes on fabrics and surface chemical composition analysis of fabrics was investigated by X-ray photoelectron spectroscopy [6].

In another research of Pei and et al., the influencing factors of shading dye deposition were found out. The more hydrophobic the fiber surface, the less dye accumulates on the fabric during washing [7].

In this study, determine to whiteness index of washed fabrics, preliminary tests were made keeping one of two components constant and changing the other. Optimum usage rate of each components was determined by spectrophotometric measurement of whiteness index after 10 washing cycle. The results of the comparison of the different ratios of the two components (percarbonate as bleaching particle; Direct Violet 9, Dispers Violet 28 as shading dyes) in detergent were given. The base powder detergent in which not contained bleaching system and shading dyes is specially prepared. Two types of detergent formulas (expressed as X and Y) were prepared by changing the amount of percarbonate and different shade dye. Percarbonate is the bleaching particle of the bleaching system in the detergent. DV9 (Direct Violet 9®) and DV28 (Disperse Violet 28®) were chosen for the shading dye. These dyes deposit onto fabrics after multiple washes and called build-up dyes. DV9 (Direct Violet 9®) is bis-azo direct dyes [11] and DV28 (Disperse Violet 28®) is anthraquinone dyes [12]. These shading dyes rapidly dissolve in water during the washing, and the dye particles rapidly deposit dye onto the fabric without causing dye damage such as spot staining [4] Furthermore these dyes is equally useful for cotton and synthetic fibres and not excessive build up on other synthetic fibres, such as polyamide.[13]

Polyamide fibers are used widely in the field of general clothing applications such as stockings, undergarments, and sportswear because they have excellent characteristics in terms of their unique softness, high strength, color development in dyeing, heat resistance, hygroscopicity and the like [14]. Also, it is widely used in women's hosiery and lingerie due to its high elongation and excellent elastic recovery quality [15]. After multiple washing, it is often observed complaint of graying/yellowing on white underwear which made by polyamide fabrics.

The aim of this research is investigation of usage of shading dyes for preventing of the complaint of graying/yellowing occurring after multi washing process in polyamide fabrics because polyamide fabrics are determined to be one of the most used fibers [16,17] and they are problematic in manner of the complaint of graying/yellowing occurring after multi washing process in polyamide fabrics. For this reason, it was searched whether the shading dye had similar whiteness performance on polyamide textiles or not, when the amount of percarbonate was reduced. In this way, reducing the bleaching system in the detergent formulation will provide some decreases in detergent production costs, CO_2 release to the environment and fabric damage.

The washing load of the study consisted of different textile fibers such as cotton, cotton-polyester, polyester and polyamide and they were washed as 25 repetitions with the prepared detergent formulations. After the 5^{th}, 15^{th} and 25^{th} washing cycles, these fabrics were evaluated in terms of washing effects. In this paper, results of washing effects on polyamide fabrics were explained. The results were assessed by the SAS 9.4 statistical program that use LSD values and sorted alphabetically.

The LSD test is used to determine whether the differences between the arithmetic mean of the measurements are statistically significant and in which groups the differences are significant.

LSD is the least significant difference, based on the calculation of confidence intervals for differences between groups.

According to the SAS software, taking into account the least significant difference (LSD) in the 95% confidence interval is sorted alphabetically (A, B, C, etc.) in terms of the arithmetic average of the compared parameters.

The letters are used to express the statistical difference between the compared values in the SAS program. For example, when A is used for one of the compared values, B is used for the other, it is stated that A is statistically significantly better than B.

MATERIAL AND METHOD

In the study 100 % polyamide knitted fabric was used as the main fabric. The mass per unit area is 135 g/m^2 [18]. The properties of used knitted fabrics are 20 course/cm in course direction and 14 wale/cm in wale direction [19]. Yarn count is 71/1 Ne [20].

The whiteness degree of fabrics (WI CIE) was measured according to ASTM E313 standard [21] by HunterLab UltraScan Pro Spectrophotometer under a D65 light source. Measurements were done for an area of 30 mm in diameter and a 10° observer. For each sample, whiteness measurements were done by 10 repetitions.

Bursting strengths were tested according to EN ISO 13938-1: 2002 (Part 1) standard [22] with 5 repetitions by using TMI instrument.

Morphological changes on the surface of the fabrics were observed using a Quanta 250FEG SEM at a typical accelerating voltage of 15 kV. Fabric samples were gold coated using a Emitech K550X sputter coater before the SEM images.

X-ray photoelectron spectroscopy was used to investigate the chemical composition of the fabric surface. Thermo Scientific K-Alpha brand device is equipped with a monochromatic X-ray source (Al Kα, hm = 1486.68 eV) with a spot size of 300 μm and 26.04 W (12.4 kV x 2.1 mA) power. High resolution spectra of the most abundant elements were obtained using pass energy of 50 eV with a spectral resolution of 0.5 eV. All measurements were conducted inside an UHV chamber with pressure at 10-6 Pa (10-8 mbar). X-ray photoelectron spectroscopy (XPS) was employed for surface chemical composition analysis of polyamide fabrics at about 10 nm depth.

FTIR-ATR spectroscopy was used to analyze the chemical composition and functional groups on the surface of the fabrics. Infrared spectra were recorded with a PerkinElmer Spectrum 100 in ATR mode.

Chemicals, detergent formulas, washing parameters used in experiments are given respectively in Table 1, Table 2 and Table 3.

Table 1. Chemicals used in the experiments

Chemicals	Brand
Base Detergent Powder	UNILEVER
DV9 (Direct Violet 9®)	BASF
DV28 (Disperse Violet 28®)	BASF

Table 2. Detergent ingredients used in the experiments

Ingredient (%)	X	Y
Direct Violet 9	-	0,25
Disperse Violet 28	0,0105	-
Percarbonate	10	12

RESULTS AND DISCUSSION

Whiteness Evaluation

Under D65 light source corresponding to daylight, accepting unwashed sample as reference, the whitening index difference (∆WI CIE) of washed sample were measured by HunterLab UltraScan Pro Spectrophotometer.

Difference of whitening index of washed polyamide fabrics (∆WI CIE) were compared by each other with SAS statistic program and the results are given in Table 5 and Figure 1.

Table 3. Washing parameters

Washing Machine:	Miele W1935 WPS EcoLine
Temperature:	40°C
Water Hardness:	20 °FH (Ca:Mg = 2:1)
Washing Program:	AutomaticPlus (≈ 90 min)
Washing Load:	3 kg (4 pcs SBL2004 Test Fabrics+Woven/Knitted, White Fabrics)
Repeat	5, 15, 25
Detergent Dosage:	150 g
Batch Ratio:	1 kg washing load :5 L washing water

Table 4. Color coordinates and whiteness index values of unwashed polyamide fabrics.

Unwashed	L*	a*	b*	WI CIE
Knitted Polyamide	94,24	-0,59	4,37	65,82

Table 5. Statistical evaluation of the difference of whiteness index of knitted polyamide fabrics (ΔWI CIE= ΔWI CIE_{washed} -ΔWI $CIE_{unwashed}$)

ΔWI CIE	LSD	Y	X	Y	X
5 th Washing	1,0472	7,4675	19,7475	B	A
15 th Washing	0,4982	11,5075	35,1125	B	A
25 th Washing	0,5468	15,1700	40,2150	B	A

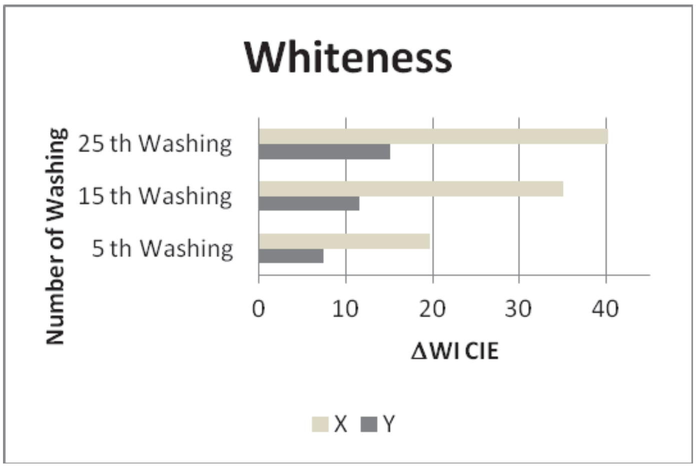

Figure 1. Graphic of the difference of whiteness index of knitted polyamide fabrics (ΔWI CIE= ΔWI CIE_{washed} -ΔWI $CIE_{unwashed}$)

Shading dyes desirably deposited on the fabric surface. Whiteness index of washed polyamide fabric with the X coded detergent including amount of 0.0105% the Disperse Violet 28 (DV28) was higher than washed with the Y coded detergent including amount of 0.25% the Direct Violet (DV9). There was 10% bleaching system in X coded detergent and 12% bleaching system in Y coded detergent. The X-coded detergent provided a higher whiteness index, although the amount of bleaching system and the amount of shading dye were less. It could be caused by the affinity to polyamide fibers of the DV28 shading dye is greater than DV9. As the result of the whiteness evaluation tests, 2% decreasing the amount of percarbonate could be tolerated by using shading dye.

Bursting Strength Evaluation

The amount of percarbonate contained in the detergents used for washings is different from each other by 2%, so this situation was investigated by bursting strength to find out the effects over fabric strength.

TSL (Tensile Strength Loss) measurements are more related to what consumers might experience in practice, as compared to the degree of polymerisation. The main drawbacks of the method are that it requires a large number of wash cycle for differences to appear and is quite laborious. Also it should be stressed that the method is only specified for use on standart white cotton, so information on the interaction of the bleach system with dyed cotton, and other materials such as viscose, polyester, polyamide can only be collected by additional research on a wider selection of textile or garments. In this case the damage done by the bleach system to woven fabrics could possibly be quantified by measuring the TSL. For other fabrics such as knitted textiles and terry cloth, bursting strength measurements are likely to provide information [23].

The bursting strength of unwashed, knitted, 100 % polyamide fabric is 1184 KPa. Bursting strength of washed polyamide fabrics were compared by each other with SAS statistic program and the results are given in Table 6 and Figure 2.

According to the results of the bursting strength test, the loss of strength after washing with both detergents was found to be equal as statistically. Statistically equivalent loss of strength by these detergents indicated that 2% reduction in the bleaching system did not make a statistically significant difference in fabric strength. The bursting strength of unwashed polyamide fabric is 1184 KPa. After the first washing, no significant change in the bursting strength of the 100% polyamide fabric was observed. As the number of washings increased, the bursting strength value decreased to 993 KPa.

XPS Evaluation

XPS analysis was used to determine the surface chemical composition of the fabrics. The atomic percentages of elements for unwashed and washed fabrics are presented in Table 7. XPS survey spectra are given in Figure 3. Detailed high resolution spectra of carbon C1s peaks for unwashed and washed fabrics are presented in Figure 4.

Table 6. Statistical evaluation of bursting strength values of knitted polyamide fabrics

Bursting strength value (KPa)	LSD	Y	X	Y	X
5 th Washing	8,8115	1069,733	1077,633	A	A
15 th Washing	12,751	1013,200	1013,667	A	A
25 th Washing	9,4779	1001,100	993,200	A	A

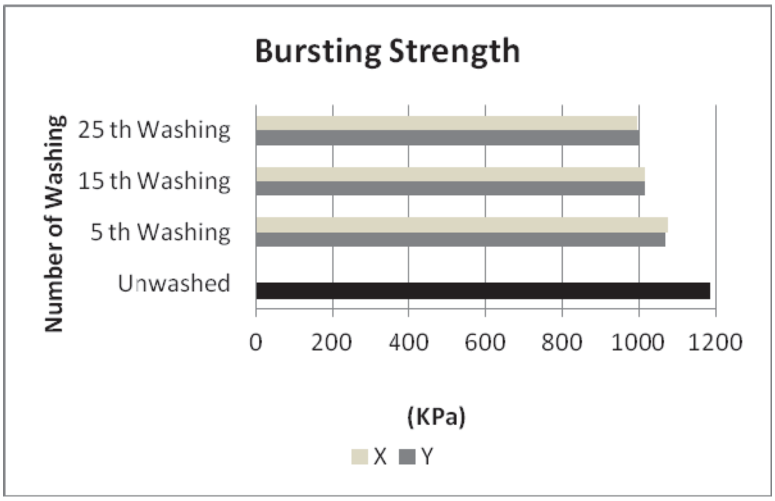

Figure 2. Graphic of bursting strength values of knitted polyamide fabrics

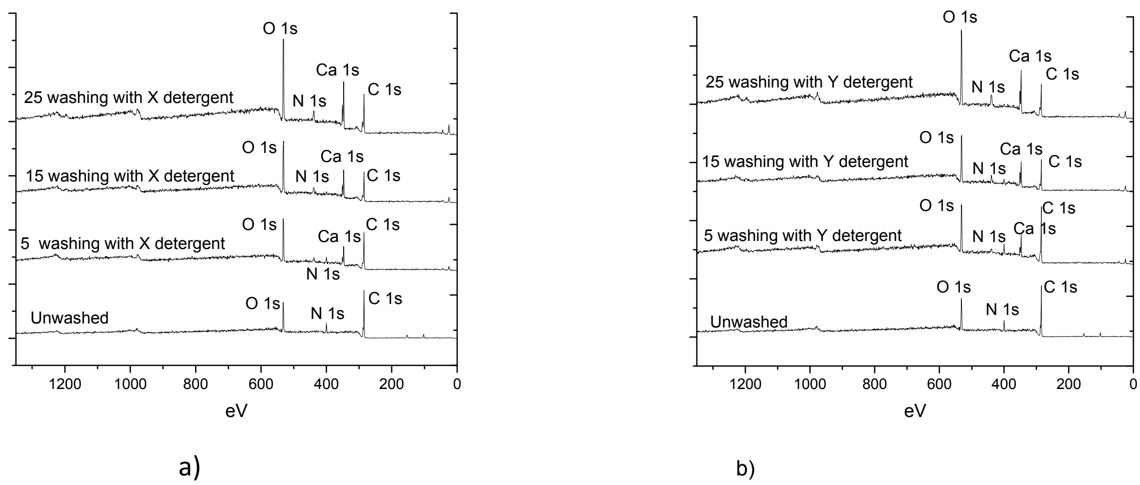

Figure 3. XPS Survey spectra of knitted polyamide fabrics a) washing with X detergent b) washing with Y detergent

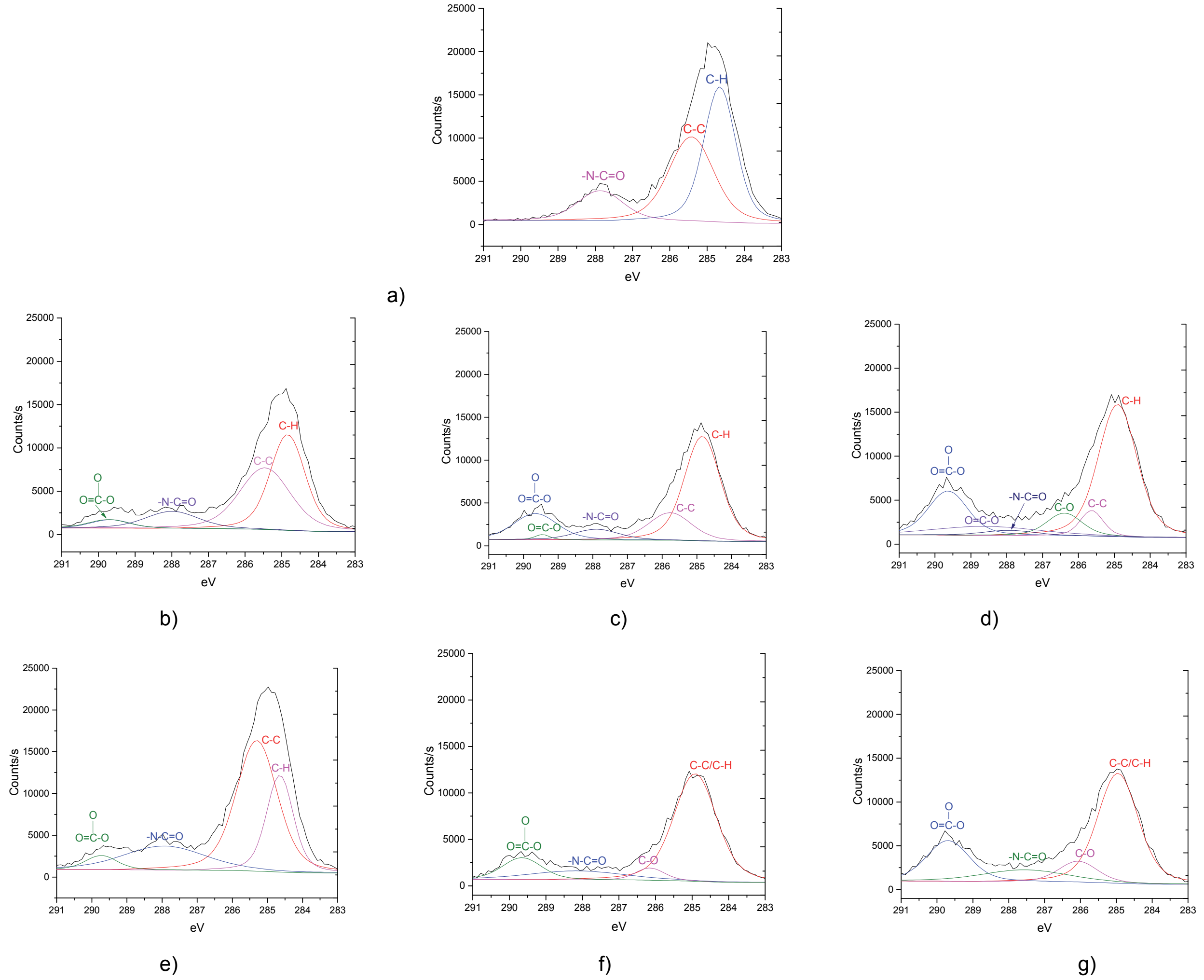

Figure 4. C1s spectra of knitted polyamide fabrics a) unwashed b) 5 washing with X detergent c) 15 washing with X detergent d) 25 washing with X detergent e) 5 washing with Y detergent f) 15 washing with Y detergent g) 25 washing with Y detergent

Table 7: Analysis results of XPS (X-ray photoelectron spectroscopy) of knitted polyamide fabrics

Atomic%	Unwashed	X Detergent			Y Detergent		
		5^{th} Washing	15^{th} Washing	25^{th} Washing	5^{th} Washing	15^{th} Washing	25^{th} Washing
C 1s	72,66	58,38	50,25	44,56	62,18	51,07	45,62
O 1s	17,22	24,62	34,37	33,96	22,62	28,40	36,01
N 1s	9,62	6,56	1,73	2,68	5,87	5,31	2,96
S 2s	-	0,54	0,59	1,38	1,49	1,53	1,26
Ca 2p	-	6,92	10,62	11,04	5,59	11,08	12,08
F 1s	-	1,88	1,44	1,06	1,22	1,83	1,17
Na 1s	-	1,1	0,99	5,31	1,02	0,77	0,9

According to XPS analysis, the results of polyamide, the elements of Ca, Na, F, S besides C, O, N elements in the polyamide structure were detected after the washing procedure. When compared unwashed and washed polyamide fabrics, the C 1s peak number increased by washing process (Figure 4). According to this, the group or element species bonded to the carbon atoms increased by washing process.

C 1s spectrums of the polyamide 6.6 fabrics were defined in details with reference to the studies of Bessada and Glampedaki in Figure 4. The chemical groups represented by peaks is shown in figure 4. In the study of Bessada et al., C 1s spectrum of the polyamide 6.6 fiber was defined peak at 285.00 eV was attributed to the C–C bonds along the polymer chain and to CH_2 groups, the peak at 286.45 eV to the C=O bond in the amide groups, the peak at 287.89 was assigned to the C atoms neighboring the amide N atom –C–NH(C=O) and the peak at 289.24 eV may be assigned to carbonyl carbons O=C–O groups [24]. In the study of Glampedaki et al, the peak at 284.83 eV was attributed C-C-C, the peak at 285.52 eV was assigned to C-C=O group, the peak at 286.25 was assigned to –C-C–N-C=O, the peak at 287.83 eV was assigned to O=C–N [25]. It was considered that the peak located around 290 eV represented the $CaCO_3$ structure. FTIR results supported that the calcium element detected by XPS on the polyamide fabric surface is the $CaCO_3$ structure.

The atomic percentage of the calcium increases for the washed polyamide fabrics. It can be said that the surface of the fabric is covered with $CaCO_3$ and this covering is also seen in SEM figures.

It is observed that the atomic percentage of the nitrogen decreases. The increase of oxygen percentage of washed fabrics is also seen in Table 7. Moreover, when the O / N ratios are examined, it is seen that this ratio increase by washing processes. It is believed that the increase in O / N ratio is due to the addition of oxygen in the carbonate structure [26] as well as oxygen in the structure of the fabric.

Sodium, calcium and fluorine elements are thought to be deposited on the fabric surface from the wash water. In addition, SBL2004 fabric used as washing load contains sodium chloride and calcium chloride. It is also conceivable that the dirt particles which suspend in the washing water during the washing process are held on the polyamide fabric surface. The sulfur element is thought to come from other components in the detergent ingredients.

SEM Images Evaluation

SEM images of polyamide fabrics before washing and after multi-washings with X and Y detergents are given in Figure 5.

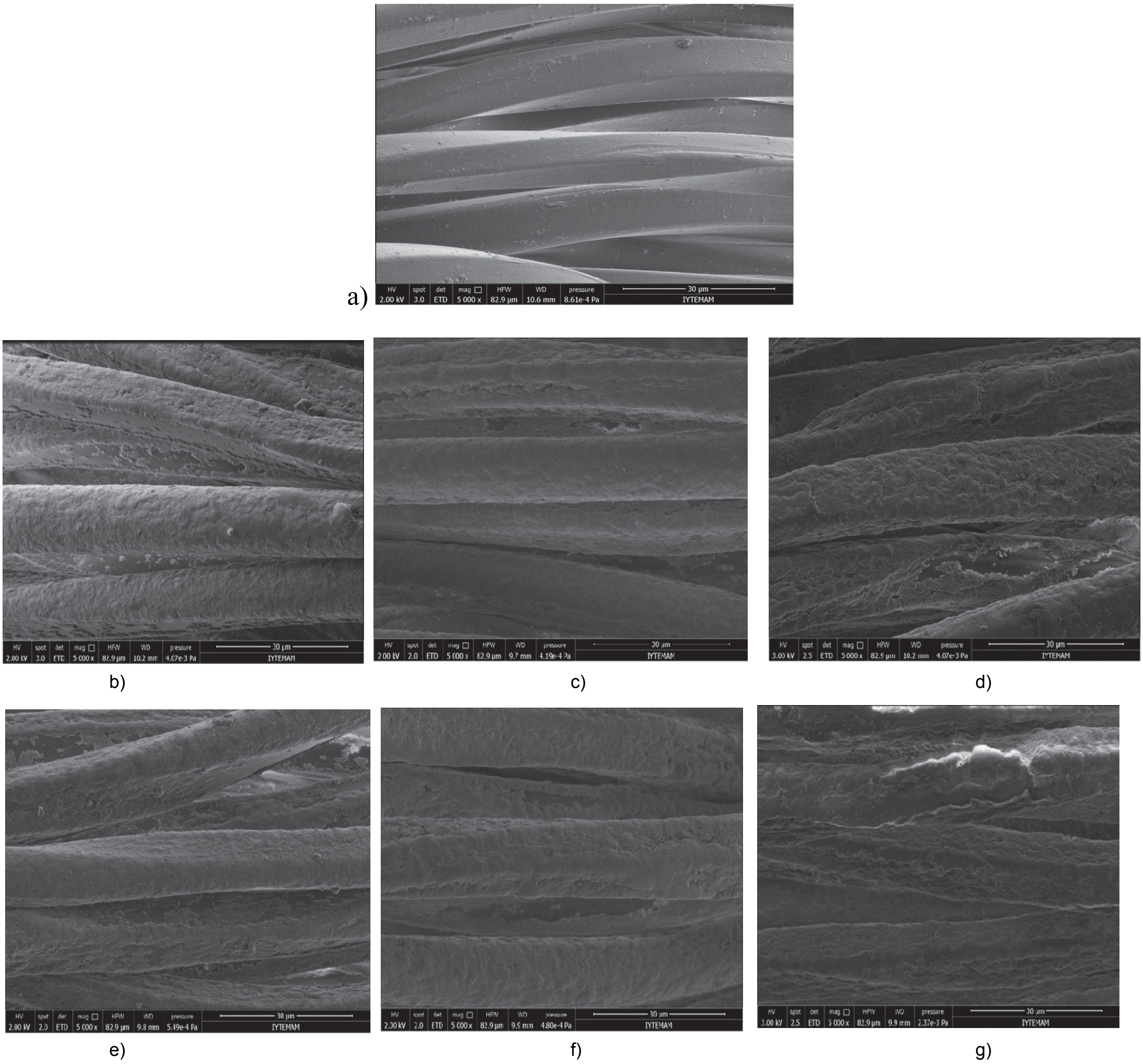

Figure 5. SEM images of knitted polyamide fabrics a) unwashed b) 5 washing with X detergent c) 15 washing with X detergent d) 25 washing with X detergent e) 5 washing with Y detergent f) 15 washing with Y detergent g) 25 washing with Y detergent

In polyamide fabrics, it is observed that surfaces of the fibers are coated after 5 washing cycles. Coating on the fiber surface increases with increasing number of washings. A similar situation is observed on fabric surface after washing with both detergents. FTIR results supported that the calcium element detected by XPS on the polyamide fabric surface is the $CaCO_3$ structure. The fabric surface coated with $CaCO_3$ is seen at SEM images.

FTIR Spectra Evaluation

FTIR spectrum of the unwashed and washed fabrics is given in Figure 6-7.

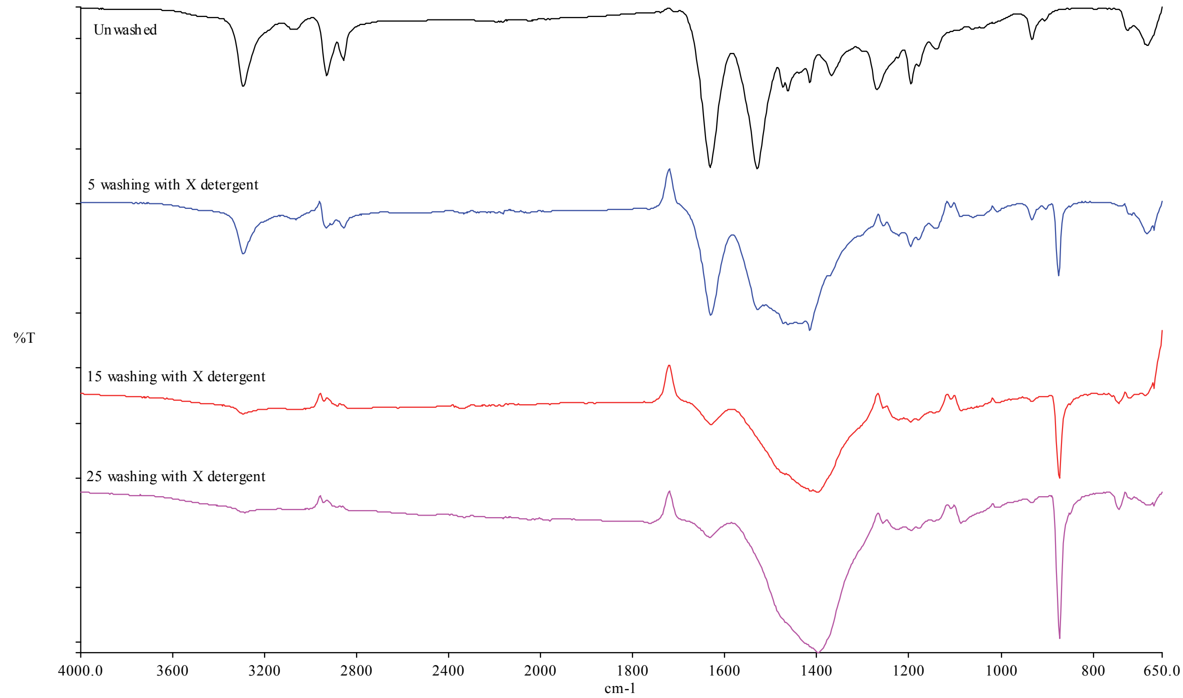

Figure 6. FTIR spectra of polyamide fabrics washing with X detergent

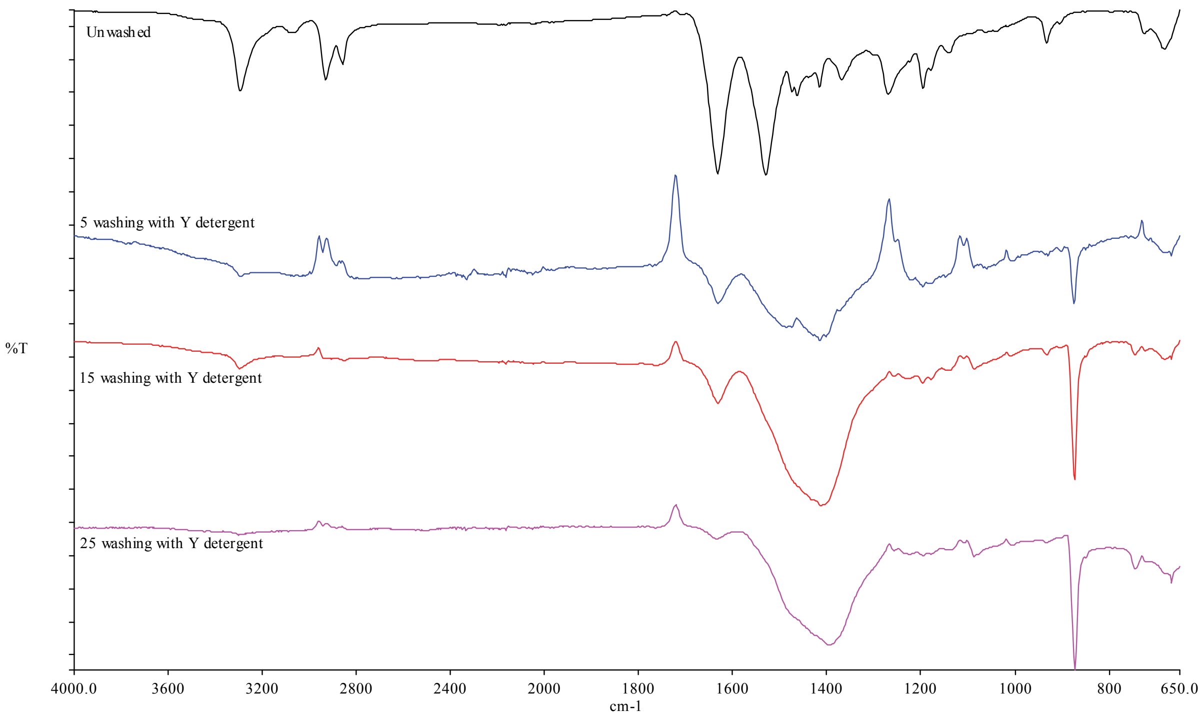

Figure 7. FTIR spectra of polyamide fabrics washing with Y detergent

The FTIR spectra of the unwashed polyamide fabric show the N-H stretching band at around 3296 cm^{-1}. The –C-H asymmetric and symmetric stretching vibrations appear at 2932 and 2859 cm^{-1} respectively [27,28]. A strong sharp band at 1633 cm^{-1} is due to C=O stretching (amide I) and a strong sharp band at 1527 cm^{-1} is due to N-H bending (amide II) [27,28,29]. The bands at 1463 cm^{-1} and 1416 cm^{-1} match with bend CH_2 vibrations [30]. The observed band at 1369 cm^{-1} is represented N-C=O (amide III) and CH_2 wagging. According to the same study, the bands at 1369, 1270 and 1196 cm^{-1} are thought to be N-C=O+CH_2 rocking vibrations [31]. It is thought that the band at 1140 cm^{-1} corresponds to angular deformation out of plane of C=O group [32], the band at 933 cm^{-1} corresponds to C-C=O stretching [30].

The FTIR spectra of the washed fabrics show a significant change. It is seen that the N-H bending / C-N stretching peak of the amide bond which is observed at 1527 cm^{-1} in the unwashed polyamide fabric is deformed and increased spectral density and peak density after the washing processes. In this case, it is considered that the C-N and C (O) -N-H bonds of the primary or secondary amines given as amide II bond in the literature are increased.

Besides, all of washed polyamide fabrics are observed forming sharp peaks at 873-876 cm^{-1} regions. According to the literature, the peak observed in this region belongs to calcium carbonate [33]. This $CaCO_3$ peak is also confirmed by the spectral screening library of the FTIR.

Density of N-H stretching band at around 3296 cm^{-1} and density of –C-H asymmetric and symmetric stretching vibrations appear at 2932 and 2859 cm^{-1} at unwashed polyamide fabric are decreased with increasing number of washing.

Also, both of FTIR spectra results and XPS analysis supported that -$CaCO_3$ is bonded on the fabric surface.

CONCLUSIONS

During the first step of the study, the optimum usage rates of the shading dyes were determined by keeping the amount of percarbonate constant and changing the proportions of the shading dyes. The rate which provided the highest whiteness index is determined as optimal rate. In the second step of the study, the amount of percarbonate was gradually reduced. The whiteness index was used to determine whether the shading dye had similar whiteness performance on polyamide textiles or not, when the amount of percarbonate was reduced. The aim of the work is to obtain a high whiteness index with the addition of shading dye in the event that a lower amount of percarbonate is used.

The results of this research is reducing of the bleach system without compromising whiteness by using shading dyes at different ratios in detergent formulations. Reducing the bleaching system in the detergent formulation provided decreasing detergent production costs and CO_2 release. Decreasing CO_2 release to the environment during detergent production is envisaged as a result of any decreases in the bleaching system [34].

Also, the calcium element was deposited on polyamide fabric after multiwashing. When the chemical structure of the fibers is taken into consideration, it is known that polyamide fibers have the nitrogen element. It is believed that, calcium bonded to the fiber surface via the amide bond in polyamide. For this reason, $CaCO_3$ was deposited on polyamide fabric. Also, both of FTIR spectra results and XPS analysis supported that -$CaCO_3$ was bonded on the fabric surface. The complaints of graying observed in multiwashed polyamide textiles can also be explained by this bonding.

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