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Research Article

The Effect of TiO_2 on Anthra Red B and Acid Black 194 Dyed Worsted Fabrics

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Abstract

Nano sized Titanium dioxide (TiO_2) produced by sol-gel method was applied on worsted fabrics using mini stenter before and after dyeing with Anthra red B and Acid black 194. The effect of TiO_2 on breaking strength, tear strength, seam slippage, hydrophobicity, fastness and color change of the fabrics examined comparatively by considering the application step. The effect of TiO_2 application on brightness and dyeing of the fabrics were measured using a spectrophotometer and FTIR-ATR, respectively. It was observed that TiO_2 application increased the brightness of the black colored fabrics, while it dulled the pink colored fabrics.

Keywords: Nanosized TiO_2, Self-Cleaning, Worsted Fabric, Sol-Gel Method, Dyeing.

TiO_2'in Anthra Red B ve Acid Black 194 Boyalı Kamgarn Kumaşlara Etkisi

Öz

Sol-jel yöntemi ile üretilen nano boyutlu Titanyum dioksit (TiO_2), Anthra red B ve Acid black 194 ile boyama öncesi ve sonrası mini ramöz kullanılarak kamgarn kumaşlar üzerine uygulanmıştır. TiO_2'in kumaşların kopma mukavemeti, yırtılma mukavemeti, dikiş kayması, hidrofobiklik, haslık ve renk değişimi üzerindeki etkisi, uygulama aşaması dikkate alınarak karşılaştırmalı olarak incelenmiştir. TiO_2 uygulamasının kumaşların parlaklığı ve boyanması üzerindeki etkisi, sırasıyla spektrofotometre ve FTIR-ATR kullanılarak ölçülmüştür. TiO_2 uygulamasının siyah renkli kumaşlarda parlaklığı arttırdığı, pembe renkli kumaşlarda matlaştırdığı görülmüştür.

Anahtar Kelimeler: Nano Boyutlu TiO_2, Kendi Kendini Temizleyen, Kamgarn Kumaş, Sol-Jel Yöntemi, Boyama.

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1. Introduction

Titanium dioxide and organic or inorganic modified titanium dioxide find applications in the textile industry for various different purposes such as antibacterial effect, photo-catalysis, self-cleaning ([1], [2]), UV-protecting ([1], [3]), hydrophilicity, super hydrophobicity, dye degradation, water and air purifying. In addition, it is used as gas sensor, photocatalyst in solar cells, co-catalyst for cotton cross-linking and photo-stabilizator of wool [1]. Due to the many uses of TiO_2, research and applications are increasing day by day with the increase of demand. In recent years, there have been some research on positive or negative effects of various textile surfaces after TiO_2 application.

Zgura et al. examined adhesion on materials, an important parameter of deposited thin films, TiO_2 material was applied to polyester textile surface by sol-gel or sputtering methods and its adhesion was examined by ultrasonic method. Despite the low application temperature, the nanoparticles showed good adhesion before and after the test [4].

Mori worked on the effect of 11 different chemicals used in dyeing and finishing processes on wool fabric handle. It was found that the fabric handle is highly dependent on the fabric structure. The study also examined the differences between the damage level of the chemicals and the hydrophilicity of the wool fiber [5].

Mirkhan et al. applied titanium nanoparticles to polyester cotton fabrics to achieve white washing and self-cleaning properties. They also examined the effects of TiO_2 on gloss and transparency, as well as the effects on natural dyed textiles. By checking physical and mechanical properties of cotton fabrics at different times, changes in time-dependent effect of nano-TiO_2 were observed. In the conclusion, it was stated that TiO_2 caused more fading on white samples and the presence of TiO_2 in white samples caused a higher reflection. When the fabrics treated with TiO_2 were subjected to UV treatment, the color strength was lowered. In the TiO_2 applied painted samples, tensile strength, strength and tension within the first 48 minutes found to be higher than the samples without TiO_2. However, it was the opposite after 48 minutes [6].

Harifi and Montazer studied the effect of nano TiO_2 on dyeing behaviour of polyester fabric. The polyester fabric was applied with nano TiO_2 and subsequently painted with two different disperse dyes without a carrier. It was observed that dye adsorption and color strength of TiO_2 pretreated polyester fabrics were increased. In addition, it was proven that there was no adverse effect on the fastness properties [7].

Nazari et al. worked on optimization of nano TiO_2 pretreatment on free acid dyeing of wool using central composite design. In the study, wool acid dyeing nanotechnology was developed at a lower temperature than the boiling point without the use of acid auxiliaries. Wool fabrics were treated with TiO_2 and BTCA (1,2,3,4-butanetetracarboxylic acid) under different conditions and then dyed with 2 different wool acid dyes. Pretreatment on wool surfaces showed significantly improved absorption of acid dyes and higher fastness properties [8].

Xu et al. successfully modified Kroy-processed and the original woolen fabrics by using TiO_2/SiO_2 70:30 sol with the stabilization of BTCA. All treated and untreated fabrics were investigated by Color Measuring & Matching System and the contact angles of fabrics were evaluated. It was observed that the total color difference (ΔE) of the coated wool fabrics increased from 30.35 to 43.09 by 42% after the application of the Kroy-treatment. It was also determined that the contact angle of Kroy-finished wool fabric fell from 140.3° to 133.5° [9].

Nateri studied dyed cotton fabrics and compared the properties of these fabrics before and after treatment with TiO_2. Some of these properties were color of fabric, depth of shade etc. In addition to that characterisation studies were carried out using FESEM (field emission scanning electron microscopy) to determine the morphology of coated fabrics [10].

Ahmad et.al. studied on cotton fabric coating with dye sensitized/TiO_2 for self-cleaning and UV blocking properties. Reactive Blue-25 (RB-25) was used as a visible light scavenger for TiO_2. Characterisation of the coated cotton fabric was carried out using FTIR-ATR, UV–Visible absorption, XRD, SEM and reflectance measurements [11].

Frunza et al. investigated functionalized wool fabrics with semiconductor nanoparticles against the photodegradation of Rhodamine B. The samples coated with oxide particles were characterised using optical microscopy, XRD, SEM, TGA, UV-Vis spectroscopy and FTIR-ATR. Rhodamine B solution was applied to the fabrics by sessile drop method. After the fabrics were dried, the change on the sample surfaces were monitored by UV-vis light as the function of the time [12].

Al-Etaibi & El-Apasery investigated the effect of TiO_2 nanoparticles on cotton fabrics dyed at high temperature. Increasing self-cleaning, light fastness, anti UV and antifungal properties were obtained [13].

Kafafy et al. immobilized ZnO, TiO_2, and CuO nanoparticles onto the cotton and wool fabrics at room temperature. After pre-treatment of nanoparticles, antimicrobial activity (optical density method), color strength (K/S), colorimetric data (L*, a*, and b*), washing, rubbing, perspiration, and lightfastness of the fabrics were tested. Besides, UV blocking and self-cleaning of the pre-treated fabrics were evaluated [14].

In the literature, effects of TiO_2 on dyeing, fastness and fabric hydrophilicity were investigated on different fabrics; and adhesion properties of TiO_2 to the fabrics were observed. However, there are no comparative studies on undyed or dyed TiO_2 treated wool fabrics. In this study, nano TiO_2 was applied to 100% worsted fabric before and after dyeing with Anthra red B and Acid black 194 by sol-gel method and compared to reference fabrics. Analysis was performed to examine the surface properties of the coated fabrics. In addition, the effect of TiO_2 on breaking strength, tear strength, seam slippage, hydrophobicity, fastness and color change of the fabrics were examined comparatively by considering application step. Two different type of dyes, Anthra red B and Acid black 194, were used during these studies. The effect of TiO_2 application to the brightness of the fabrics was measured using spectrophotometer and the effect of TiO_2 presence on dyeing of the fabrics was observed using FTIR-ATR.

2. Material and Method

2.1. Material

Acetic Acid (Glacial 100% EMSURE, anhydrous for analysis) and Nitric Acid 65% (extra pure) were purchased from Merck. Titanium (IV) Isopropoxide (97%) was supplied from Sigma Aldrich.

In this research using the same warp and weft yarn as 100% wool Nm 57/2 with 1100 tpm in Z direction, reed width in 192 cm, reed drawing in at 80/3 has been produced as raw color namely ecru in Yünsa by Dornier weaving machine. Weft setting fabric sample has been 24 cm^{-1} with straight draft under the same conditions. After weaving, the fabrics were washed in an open width washing machine at 55°C at a transition speed of 22 m/min. Some of the fabrics were pre-treated with TiO_2 using stenter. Then, untreated and pre-treated fabrics were processed with the Anthra red B and Acid black 194 in the wool dyeing program at 98°C for 45 minutes with the same recipe and under the same conditions. After the treatments, pink and black fabrics were successfully obtained. In addition, TiO_2 was applied to some of the untreated dyed fabrics. The performance of all fabrics in ecru, pink and black colors were tested and compared to each other.

The fabrics used in the study were pre-conditioned for 24 hours at standard atmospheric conditions (20 ± 2°C, 65 ± 2% RH). The breaking strength values were determined using Multipurpose Strength Tester, Zwick 1120, at 100 mm/min (stripe method) according to TSE EN ISO 13934-1. The seam slippage strength of the fabrics were determined according to TS EN ISO 13936-1 using Multipurpose Strength Tester, Zwick 1120.The tear strength of the fabric samples were measured using Zwick 1120 strength tester according to TS EN ISO 13937-1. The contact angle of the fabric samples were measured according to ASTM 7490-13. The FTIR spectra were acquired using Agilent Cary 630 FTIR-ATR spectrophotometer in the range of 650-4000 cm^{-1} spectral region. Color measurement and brightness values were determined using CIE*a*b system as D65-10 measurement with Datacolor 800.

The rubbing fastness evaluation were carried out using the grey scales according to TS EN ISO 105 X12. The test results of the perspiration fastness values for acid and alkaline were determined according to TS EN ISO 105 - E04 standard. The dry cleaning and the water fastness were evaluated according to TS 473 EN ISO 105 D01 and TS EN ISO 105 - E01, respectively.

2.2. Method

2.2.1. Preparing of Sol-Gel

TiO_2 was prepared by sol-gel method in chemistry laboratory of Yünsa. A beaker filled with distilled water and heated up to 80^0C. While stirring the solution vigorously with mechanic stirrer at 1200 rpm, Acetic Acid, Nitric Acid and Titanium (IV) Isopropoxide (TTIP) were added respectively. Stirring continued until a homogeneous and transparent solution was obtained [15].

2.2.2. Application Method

Application of the prepared solution to the fabrics was performed using mini stenter which was placed in the finishing department of Yünsa. Washed and dried fabrics were passed through the solution diluted in the ratio of ½. After squeezing at 7.5 bar pressurised cylinder, they were passed through at 180^0C drying and fixation cabin with 1 m/min velocity. The velocity of fans were set at 1800 cycle/min.

3. Results and Discussion

The effect of the application on the breaking strength for all the fabrics can be seen in Table 1. In addition to having no adverse effect of the application on seam slippage, there was only a slight increase in either direction. TiO_2 application had a negative effect on tear strength values for both pre-treated and post-treated black fabrics on warp direction, and post-treated pink fabric on weft direction. When all the contact angle test results were considered, only the result of the post-treated black fabric obtained lower than the others.

To examine the effect of dye binding of TiO_2, change of color fastness tests were carried out and all test results were found to be as required shown in Table 2. The lighter color, pink, gave the better fastness results as expected. It was observed that the application did not have a significant effect on the rubbing fastness. In other fastness tests, it was observed that it had a negative effect of 1 degree, especially on pre-treated fabrics in both colors.

TiO_2 application caused all fabrics to lighten as expected. Although pre-treated pink fabric was lighter in color than post-treated pink fabric, the opposite effect was observed in black fabrics. Considering the Da* and Db* values, it was observed that the application made the fabrics more green and blue; the highest change was observed in pre-treated pink fabric. When DC* values were interpreted, it was observed that TiO_2 application increased the brightness in black colored fabrics, while it dulled the pink colored fabrics. It was determined that pre-treated pink fabric was duller than post-treated pink fabric and the brightest fabric among the fabrics was post-treated black fabric. DE value was above the acceptable limit (≤1) in the both pre-treated pink and post-treated black fabrics (Table 3).

Chemical surface modification of the wool fabric coated with two different dyes and TiO_2 were studied by FTIR-ATR. The first band is the broadest and is observed at around 3400-3100 cm^{-1} corresponding to the stretching vibration of the -OH and -NH groups.

Two bands at around 1510 cm^{-1} and 1625 cm^{-1} are related to the amide groups of the wool material and when the wool fabric was treated with dye or TiO_2, the intensity of the band decreased which shows chemical bonding occurrence. When the dye application was carried out before TiO_2 application, the intensity of the peaks is lower compared to the peaks of the untreated fabrics. When the TiO_2 application is before the dyeing application, the intensity of the peaks lowers less. These values can be seen in the Figure 1 and 2.

Table 1. The technical properties of sample fabrics

Test	Width	Weight	Breaking Strength (warp)	Breaking Strength (weft)	Seam Slippage (warp)	Seam Slippage (weft)	Tear Strength (warp)	Tear Strength (weft)	Contact Angle
Unit	cm	g/m^2	daN	daN	kg	kg	gf	gf	deg.
Standard	-	TSE 251	TS EN ISO 13934-1	TS EN ISO 13934-1	ISO 13936-1	ISO 13936-1	ISO 13937-1	ISO 13937-1	ASTM 7490-13
Untreated / ecru	154	192	32	20	>20	12	2686	1754	130
Treated / ecru	153	200	35	23	>20	18	2752	1623	126
Untreated / pink	154	215	31	24	19	20	2530	1865	126
Pre-treated / pink	153	208	34	25	>20	18	2442	1902	128
Post-treated / pink	150	213	36	25	>20	>20	2683	1622	133
Untreated / black	142	226	33	23	20	15	3021	1529	131
Pre-treated / black	143	239	39	25	>20	20	2687	1698	134
Post-treated / black	147	219	36	26	>20	>20	2685	1542	115

Table 2. Change color of fastness of the fabrics

Test	Rubbing Fastness (dry)	Rubbing Fastness (wet)	Perspiration Fastness-Acid	Perspiration Fastness-alkaline	Dry Cleaning Fastness	Water Fastness
Unit	Color Change	Color Change	Color Change	Color Change	Color Change	Color Change
Standard	TS EN ISO 105-X12: 2006	TS EN ISO 105-X12: 2006	TS EN ISO 105 E04	TS EN ISO 105 E04	TS 473 EN ISO 105 D01	TS EN ISO 105 E01
Standard	≥3.5	≥2.0	≥4.0	≥4.0	≥4.0	≥4.0
Untreated / pink	4.5	4.0	5.0	5.0	5.0	5.0
Pre-treated / pink	5.0	4.5	4.0	4.0	4.5	4.5
Post-treated / pink	5.0	4.0	5.0	5.0	5.0	5.0
Untreated / black	3.0	2.0	4.5	4.5	4.5	4.5
Pre-treated / black	3.5	2.5	4.0	4.0	4.0	4.0
Post-treated / black	3.0	2.0	4.5	4.5	4.5	4.5

Table 3. The color value changes on the spectrophotometer after TiO_2 application

Sample	DL*	Da*	Db*	DC*	CMC dE	Result
Pre-treated / pink	4.00	-4.92	-1.18	-4.66	3.00	Fail
Post-treated / pink	0.40	-0.95	0.07	-0.95	0.47	Pass
Pre-treated / black	0.26	-0.02	-0.17	0.16	0.36	Pass
Post-treated / black	1.07	-0.09	-0.53	0.51	1.31	Fail

	DL*	Da*	Db*	DC*
+	lighter	more red	more yellow	brighter
-	darker	more green	more blue	duller

CIE*a*b system with D65-10 measurement

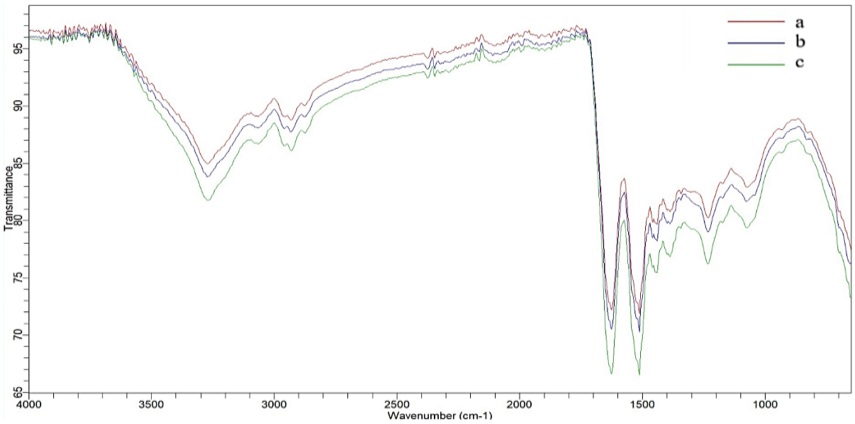

Figure 1. FTIR spectrums of pink colored fabrics which TiO_2 was applied to a) treatment after dyeing, b) treatment before dyeing, c) untreated

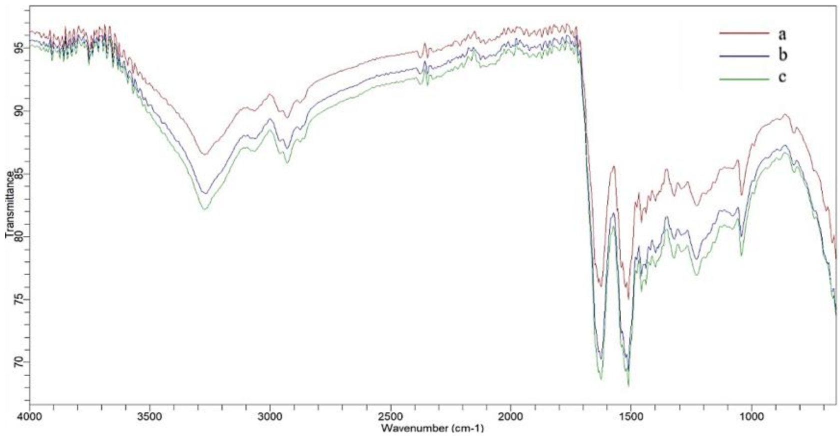

Figure 2. FTIR spectrums of black colored fabrics which TiO_2 was applied to a) treatment after dyeing, b) treatment before dyeing, c) untreated

4. Conclusions and Recommendations

In this study, nano-sized TiO_2 was applied to 100% worsted fabric before and after dyeing with Anthra red B and Acid black 194 by sol-gel method and compared to reference fabrics.

DE value was obtained above the acceptable limit (≤1) in the both pre-treated pink and post-treated black fabrics. As the dyeing process performed before TiO_2 application, the intensity of the peaks is the lowest and for untreated is the highest at FTIR spectrum. The fastness test results could not be correlated with logical explanations. However, spectrophotometer test results based on the color evaluations performed. The dullest was obtained for pre-treated pink fabric but the brightest color for the post-treated black fabric.

It is seen that nano-sized TiO_2 application to 100% worsted fabric before and after dyeing affects the color shades. It was observed that this situation changes from color to color; so more experiments can be carried out on the worsted fabrics dyed with different colors in the future studies.

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