### The Effect of TiO2-SiO2 Nanocomposite on the Performance Characteristics of Leather

#### Meruyert Koizhaiganova Kaygusuza\*, Michael Meyerb, Ahmet Aslanc

<sup>a</sup> Denizli Vocational School of Technical Sciences, Pamukkale University, 20013, Denizli, Turkey
 <sup>b</sup> Research Institute of Leather and Plastic Sheeting - FILK, Freiberg, Germany
 <sup>c</sup> Leather Engineering Department, Engineering Faculty, Ege University, Bornova, Izmir, 35100, Turkey

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In this study the effect of TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite on various performance characteristics of finished leather was investigated. For this purpose, TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite was prepared via the sol–gel method from tetraethoxysilane (TEOS) and titanium n-butoxide (TBO) catalyzed with acid at ambient temperature. The prepared composite was applied by spraying on to the top coat of finished leathers. Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) were employed to characterize the surface properties and the chemical structure of the nanocomposite films. Inductively coupled plasma optic emission spectrometer (ICP-OES) was used to evaluate elemental analysis of the nanocomposite on leather. The physical-mechanical and fastness properties of leathers treated with the nanocomposite were evaluated according to appropriate standards. The results indicated that the use of TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite improved certain performance characteristics of leather such as dry and wet rubbing fastness, color fastness to UV light and finish adhesion.

Keywords: TiO,-SiO, nanocomposite, Sol-gel, Leather, Finishing, Coating

#### 1. Introduction

Leather is a natural product with its own unique characteristics, and it is also available in different qualities and finishes. The finish of leather can vary greatly, mainly depending on the purpose of the leather. The finishing process applied plays a leading role in increasing various fastness properties of leather such as hue, luster or feel and also light or rub-fastness. A finishing coating provides protection against wetness, soiling and mechanical action. At the same time, damage to the leather or grain defects is covered. Also, many fashion effects are not possible without finishing!

The sol-gel method is one of the most widely used techniques for the synthesis of functional coating films for substrate surface modification and the improvement of material properties which are affected by surface conditions. This technique possesses a number of advantages over conventional film formation techniques, including a relatively low processing temperature, ease of applying homogeneous multicomponent oxide films over large surfaces, and good control of the composition and property of the final material<sup>2</sup>.

In the leather finishing process, TiO<sub>2</sub> is generally used as a pigment and filler, and it is used more widely in the processing of white leather. Recently, studies have been conducted making use of the photocatalytic properties of TiO<sub>2</sub> for antimicrobial and self-cleaning coatings<sup>3-5</sup>. There are also several studies on the use of SiO<sub>2</sub> in the finishing process<sup>6-8</sup>, but a scan of the literature showed no studies on the use of composites containing both TiO<sub>2</sub> and SiO<sub>2</sub> in leather

The aim of the research was to increase the performance characteristics of finished leather using TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite produced by the sol-gel method in the finishing process.

#### 2. Experimental

#### 2.1. Materials

Tetraethyl orthosilicate (TEOS) was purchased from Aldrich. Titanium n-butoxide (TBO) was provided by Merck. All materials were used as received. Distilled water was used for the hydrolysis of alkoxides and acetic acid (100%) was used as a catalyst. Ethyl alcohol (Merck) of analytical grade was the solvent for the sol. Acetylacetone was used to stabilize the colloidal solution of TiO<sub>2</sub>-SiO<sub>2</sub>. Garment crust leathers (goat, brown color) were used in the study. Nitrocellulose lacquer (EL 8081) was provided by Verpol (Turkey). Nitrocellulose lacquer is a finishing material which is made of nitrocellulose combined with other resins dissolved in lacquer thinner solvent (water in our case).

## 2.2. Application of the prepared TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite to leather

The preparation and characterisation of TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite were carried out as described in Ref.<sup>9</sup>. In

finishing. The present study was undertaken considering the possibility of making use in the leather finishing process of the properties and contained in the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite.

<sup>\*</sup> e-mail: meruyert\_k@hotmail.com

brief, the amounts of required ethanol, acetic acid, distilled water and TEOS were mixed in the round-bottomed flask with stirring condition. Afterward, a calculated amount of TBO (to obtain 50/50 mol ratio % of TiO<sub>2</sub>/SiO<sub>2</sub>) was added into this solution drop by drop and the mixture was stirred for 30 minutes to complete hydrolysis process of SiO<sub>2</sub> and TiO<sub>2</sub>. The ultrasonic treatment was applied under 15 kW power. The final transparent sol was then aged for 24 h. The composite solution had a pH value of 5.2, viscosity of 1-3 mPa.s, turbidity value of 12.7 ntu and particle size of approximately 6 nm.

In our study, we use the same proportion of TiO<sub>2</sub> and SiO<sub>2</sub> in the composite in order to observe the effect of both materials on the performance characteristics of the treated leather. The prepared nanocomposite was applied to the leather as follows. Applications were carried out on leathers through a standard finishing method based on hand-spraying with a compressed-air gun. The base coat and dye coat (pigment coat) were applied by the conventional method. The TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite was applied by spraying on to the top coat of the finished leathers (except in the control 1 samples without treatment and control 2 samples treated with lacquer) in the three following variations:

- (1) K (nanocomposite): The required amount of nanocomposite was sprayed on the surface in two crosses, then the samples were hung up to dry for five minutes and press-ironed at 95°C for three seconds.
- (2) K+L (nanocomposite + lacquer): The required amount of nanocomposite was sprayed on to the surface in two crosses, followed by spraying with a mixture of nitrocellulose lacquer on to the surface in two crosses and hanging up the samples to dry for five minutes and press-ironing at 95°C for three seconds in between each spraying.
- (3) L+K+L (lacquer + nanocomposite + lacquer): Nitrocellulose lacquer was sprayed on the surface in two crosses, and then the nanocomposite and nitrocellulose lacquer were sprayed on the surface in two crosses, and the samples were hung up to dry for five minutes and press-ironed at 95°C for three seconds in between each spraying.

# 2.3. Characterization and determination of performance properties of leathers treated with TiO<sub>2</sub>-SiO<sub>2</sub>, nanocomposite

Samples were tested three days after treatment. All samples were conditioned in controlled laboratory conditions (23±2°C, 50% RH) for 24 h before any measurements were performed with regard to ISO 2419:2012¹¹¹. The surface morphology of the leather was examined using a scanning electron microscope (SEM, Philips XL-30S FEG). FTIR analysis was conducted in order to determine the differences in the chemical properties of leather treated with nanocomposite and untreated leather. FTIR studies were carried out on a Spectrum 100 device with ATR equipment (Perkin Elmer,

USA). For this purpose, the leather samples were scanned with IR spectra at a wavelength of 4000-400cm<sup>-1</sup> and the results were evaluated with FTIR Spectrum Software. An inductively coupled plasma optic emission spectrometer (ICP-OES, Perkin Elmer, USA) was used to evaluate elemental analysis of the nanocomposite on leather.

Performance tests carried out on the manufactured leathers were as follows. Measurement of rubbing fastness (wet and dry) of leathers was performed according to ISO 11640:2012<sup>11</sup>. This method is intended for determining the transfer of colour and the behaviour of the surface of a leather on rubbing with an undyed wool felt (wet or dry).

Colour fastness to water and perspiration was determined with reference to ISO 11642:2012<sup>12</sup> and ISO 11641:2012<sup>13</sup>. Samples of leather and textile fabrics, e.g. CA = acetate, CO = cotton, PA = polyamide, PES = polyester, PAC = Polyacrylic, WO = wool, are thoroughly wetted out separately in a water or an artificial perspiration solution. The textiles are placed on the side of the leather specimen to be tested and the composite specimen is then placed between glass plates under pressure for 3 hours at 37°C, then dried.

Colour fastness to light and UV light were performed with regard to ISO 105-B02:2014<sup>14</sup> and ISO 105-B04:1994<sup>15</sup>. This method is intended for determining the resistance of the colour of leather to the action of a standard artificial light source (Xenon lamp) or UV light.

The change in colour of the leather or textile in rubbing fastness and colour fastness tests are assessed with a standard Grey Scales. The scale has the 9 possible values (from best to worst rating): 5, 4-5, 4, 3-4, 3, 2-3, 2, 1-2, 1, each representing a visual difference and contrast.

The Measurement of the adhesion of the finish to leather or the adhesion between two adjacent layers of the finish was done in accordance with ISO 11644:2009<sup>16</sup>. The finish side of a strip of leather is first stuck to a test strip using an adhesive which does not affect the bond of the finish to the leather material. Increasing static loads are applied to the material until it peels away, leaving the finish on the test strip.

The resistance of leather to flexing movements or flex resistance test was done using a bally flexometer according to ISO 5402- $1:2011^{17}$ . Leather specimen of dimension  $70 \times 45$  mm is folded and fixed to the jaws of the instrument in such a manner that the grain side remained outside with fold on the specimen. The motor is switched on having one clamp fixed and the other moved backward and forward causing folds in the specimen to run along it.

Determination of resistance to grain cracking and grain crack index was carried out using a lastometer in accordance with ISO 3378:2002<sup>18</sup>. A disc shaped specimen of the leather is firmly held with the grain side up between the clamping rings, with the spherical tip of the steel rod just touching the flesh surface. The specimen is moved downward against the rod, distending the grain of the leather immediately above

the rod, while the surface is watched for incipient cracking and bursting.

#### 3. Results

#### 3.1. Characterization of the leather samples

FTIR spectra of the leather samples were taken in order to determine the chemical changes taking place in the control leather samples and those coated with the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite solution (Figure 1). Table 1 show the FTIR spectra and the functional groups obtained as a result of the FTIR scans. All of the functional groups of the chromium crust leathers were observed in the FTIR spectra of all leather samples<sup>19</sup>. However, in the spectra of the control samples treated with lacquer, a difference in prominence was observed in various peaks. Examining the spectra obtained after spectral scanning, the bands emerging in relation to stretching vibration of the (0) C-O, (1) C-O-C, (2) OR-C-C, (3) COO-CH<sub>2</sub> (asymmetric), (4) C=C, (5) C=O, (6) -CH<sub>2</sub> and (7) -CH<sub>3</sub> groups on the structural chain of the control leather samples and those treated with nanocomposite were found to be at wavenumbers of (0) 1020, 1082 (1) 1064, (2) 1140, 1174, (3) 1454-1457, (4) 1633-1645, (5) 1723,1724, (6) 2854-2857 and (7) 2924-2926 cm<sup>-1</sup> respectively (Table 1). In all samples, peaks of 1233-1281 cm<sup>-1</sup> and 1336-1378 cm<sup>-1</sup> were established as amide band I, and peaks of 1552-1555

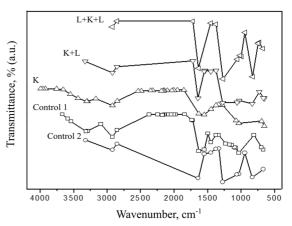


Figure 1. FTIR spectra of the leather samples.

cm<sup>-1</sup> as amide band II<sup>20</sup>. In addition, it was determined that the peak of 655-680 cm<sup>-1</sup> was from the Ti-O stretching mode and that peaks of between 3316-3332, 3543-3589 cm<sup>-1</sup> and 3657-3671 cm<sup>-1</sup> were from the O-H stretching mode<sup>21,22</sup>. As shown in Table 1, the clearest peaks were observed for the SiO- group bond at a wavenumber of 999 cm<sup>-1</sup>, and at 1540 cm<sup>-1</sup> for the Si-O-R bond<sup>23</sup>. At the same time, peaks of Ti-O-Ti were determined in the leather samples at a wavenumber of 746 cm<sup>-1</sup> and at 946-947 cm<sup>-1</sup> peaks of Si-O-Ti<sup>24</sup>,<sup>25</sup>. It was proposed that TiO<sub>2</sub> can form strongly hydrogen bond with collagen<sup>4</sup>, while Si-OH groups could react with the

Table 1. Main functional groups in FTIR spectra.

Functional groups	Control 1	Control 2	K	K+L	L+K+L
Si-O	671	669	655	655	680
C-O	1035	1032	1035	1028	1020
C-O	1082		1082		
C-O-C		1064		1064	1063
OR-CC	1140, 1174				
C-N	1233	1277	1281	1277	1274
C-N	1336	1337	1339	1337	1336
C-N	1378	1376	1376	1376	1378
COOCH3	1454	1454	1452	1455	1457
N-O	1552	1552	1553	1555	
C=C	1633	1642	1633	1645	1639
C=O	1723			1724	1724
- CH2	2854	2855	2854	2856	2857
- CH3	2924	2924	2923	2924	2926
-OH	3316	3323	3316	3332	
-OH	3589	3543	3553		
-OH	3671		3657		
TiOTi					746
SiOTi			947	946	946
SiO					999
SiOR				1540	

pendant groups of arginine, histidine and tryptophane to form -Si-C- bond, condense with pendant hydroxyl groups of collagen and form hydrogen bond with C=O and N-H groups of collagen<sup>26</sup>. According to the obtained FTIR spectra it can be concluded that the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite has been bonded to the surface of the treated leathers and thus, a finishing coating should be formed.

After finishing, imaging of the finishing layer on the surface of the leather was performed by scanning electron microscope (SEM). Figure 2 shows the SEM surface images of the control leather samples and those treated with the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite solution at a magnification of x1000. It was observed from the SEM images that the surface of control 1 leather sample had a natural appearance with clear scratches and pores and that on the surface of control 2 leather sample (treated with lacquer) the film was rough (Fig. 2a,b); only in the films formed on the surface of the leather sample treated with the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite (K) did cracks occur (Fig. 2c), while the films on the leather sample treated with composite and lacquer (K+L) and the sample treated with a double coat of lacquer and composite (L+K+L) were more homogeneous, smooth and without cracks (Fig. 2d,e).

Table 2 shows findings relating to Ti and Si from the ICP-OES analysis. As seen in the Table, Si was found in the small amount of 7.2 ppm in the control 1 leather, while in control sample 2, it was found at 32.4 ppm. This shows that Si was present in the leather samples used, arising from the operations before finishing. It also shows that Si existed as an impurity in the lacquer used. The element Si is not used directly in the stages of leather processing, but it is thought that it may be included in the leather structure from impurities in chemicals used in the production process. Ti was not detected in either of the control leather

Table 2. Si and Ti contents in leather samples.

Sample	Si, ppm	SD	Ti, ppm	SD
Control 1	7.2	0.6	0	0
Control 2	32.4	0.3	0	0
K	54.4	0.1	43.8	0.3
K+L	98.1	0.1	147.4	0.8
L+K+L	149.4	0.6	250.0	0.7

samples. Comparing amounts of Si and Ti in the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite treated leather samples, it was observed that although the proportion of Ti to Si in the composite was 50/50, there was a higher amount of Ti in the K+L and L+K+L samples (147.4 and 250.0) than Si (98.1 and 149.4), but not in the K sample (Si-54.4; Ti-43.8). Also, there was the highest amount of each element in the third variation of finishing treatment. We conclude that a higher amount of both elements in K+L and L+K+L samples were detected due to the better adhesion of composite in the presence of lacquer as it was observed in SEM images as well. In spite of the same proportion, non uniform distribution of elements in the leather samples was probably due to application of the nanocomposite by spraying.

#### 3.2. Physical and fastness properties of leathers

Results of fastness and physical testing (finish adhesion, dry flex resistance, wet and dry rub fastness, color fastness to light and UV light) are given in Table 3. Examining Table 3, it is seen that the wet rubbing fastness of the control 1 leather sample and the dry rubbing fastness of the leathers (control 2) had a value of 4. At the same time, in evaluations made on the leather it was found that only the lacquer-treated control 2 sample had a low fastness value of 2/3 in wet rubbing. It was

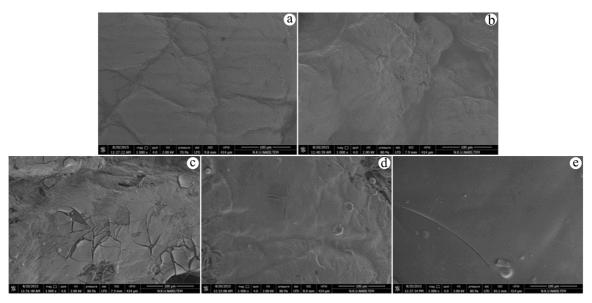


Figure 2. SEM micrographs of the leather samples (with x1000 magnification): a) control 1, b) control 2, c) K, d) K+L and e) L+K+L.

Specimen	Finishadhesion (N)	Dry rub fastness		Wet rub fastness		Color fastness	
		Leather	Felt	Leather	Felt	UV light	Light
Control 1	6.8	3/4	4	4	4	2/3	2/3
Control 2	9.6	4	4	2/3	3/4	3	3
K	9.2	3	3	2/3	3	3/4	2/3
K+L	9.7	3/4	4	3	3	3/4	2/3
L + K + L	11.1	5	5	4/5	5	4	3/4

Table 3. Physical and fastness properties of leathers.

observed that treatment only with TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite (1st variation) did not have a great effect on wet and dry rubbing fastness. The dry rub fastness of the K+L leather sample was close to that of control 1 leather sample while the wet rub fastness of this leather sample was lower than that of control 1. The L+K+L leather sample showed the highest dry rubbing fastness (5) and the highest wet rubbing fastness (4/5). This shows that the resistance to mechanical effects of the finished leather surfaces in the 3rd variation (L+K+L) was increased. In general, it was observed that the dry rubbing fastness of TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite treated leathers was better than their wet rubbing fastness property.

Table 3 shows the finishing adhesion values of the control leather samples and the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite treated samples. For control 1 and control 2 samples, these values were found to be 6.8 N and 9.6 N respectively. The finishing adhesion value of the leather sample treated with nanocomposite only (K), 9.1 N, was found to be lower than that of lacquer-treated leathers (control 2), and this value for the K+L sample, 9.7 N, was found to be a little higher than that of the lacquer-treated leather. It was determined that the L+K+L sample had the highest finishing adhesion value (11.1 N). In this way, it was determined that the best adhesion result was obtained from the value of the leather treated with the 3<sup>rd</sup> variation (L+K+L).

In order to test the flexing endurance of the finishing layer applied to the leathers, they were subjected to bending in a Bally flexometer. After bending 100 000 times, no damage was seen in the finishing layers of any of the leather samples. After this process the surface color of the leather samples was assessed and no color change was observed for any samples either.

Table 3 gives the values of fastness to light and UV light of the control and TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite treated samples. The values of control 1 and control 2 were the same: 2/3 and 3 respectively. The highest value of fastness to light was obtained for L+K+L leather samples (3/4). As for fastness values to UV light, an increase was seen in all TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite-treated leather samples compared with the control leather samples. It is thought that the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite increases the fastness values of the leathers to UV light, and that this most likely derives from the photocatalytic effect of TiO<sub>2</sub>.

Colour fastness when subjected to water and low perspiration is a constant problem for manufacturers of clothing and low values can have disastrous and costly results. Table 4 gives the values of color fastness to water of the control leathers and those finished with TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite. Color change and fastness in leathers are expressed as fading, or flow if it transfers to adjacent fabrics. Examining Table 4, it is seen that the control leathers had fastness to water values of 4, while the fastness values of the nanocomposite treated samples (K, K+L, and L+K+L) were 4/5. As Table 4 shows, it was observed that the values of fastness to perspiration of the control leathers were 4, and as with the color fastness to water, the nanocomposite treated leathers (K, K+L and L+K+L) had values of 4/5. In addition, when the control leather samples and all leather samples treated with TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite were examined, it was seen that the greatest color transfer from the leather samples was to cotton and polyamide.

Garment leathers can be exposed to the effects of pulling and stretching from many different directions. These kinds of physical effects can mostly be seen in jackets and coats at the elbows, and in pants at the knees. Lack of strength in these areas reduces the useful life of the leathers. For this reason, it is desirable to see whether any faults will emerge in the leather in the knee and elbow areas where a large amount of flexing is necessary by determining the grain cracking and grain bursting of garment leathers.

Grain cracking and grain bursting tests were performed in order to examine the behavior of the control and TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite treated leathers under multiple forces. Table 5 shows the values obtained for leather cracking strength, leather cracking elongation, grain bursting strength and grain bursting elongation. As seen in the table, cracking and bursting strengths for the control 1 and control 2 samples were found to be 149.0 and 193.4, and 220.2 and 243.8 N. While the K sample values were found to be lower than those of the control samples, it was determined that the values of the K+L samples were close to those of the control samples. In this group, the highest values of crack strength and burst strength were found in the L+K+L samples (225.4 and 291.5). In this way, in a general assessment of all of the samples, it was seen that the best results were obtained from the L+K+L group.

Table 4. Color fastness to water and perspiration.

		Color fastnes	ss to water		
	Control 1	Control 2	K	K+L	L + K + L
Acetate	3	3	3/4	3	2
Cotton	2	2/3	3	2/3	2
Polyamide	1/2	1	1/2	1/2	1/2
Polyester	3/4	3/4	3/4	3/4	4
Polyacrylate	4	4	4	3/4	4
Wool	2	2/3	2/3	2	3/4
Leather	4	4	4/5	4/5	4/5
		Color fastness to	o perspiration		
Acetate	1	1	2	1/2	1
Cotton	1	1	1	1	1
Polyamide	1	1	1	1	1
Polyester	1	1	2/3	1/2	1/2
Polyacrylate	1	1	2/3	1/2	1/2
Wool	1	2	1/2	1/2	1/2
Leather	4	4	4/5	4/5	4/5

Table 5. Grain cracking and grain bursting strength values.

Specimens	Crack strength, N	Crack elongation, mm	Burst strength, N	Burst elongation, mm
Control 1	$149.0 \pm 0.4$	$12.3\pm0.1$	$220.2\pm0.6$	$14.9 \pm 0.1$
Control 2	$193.4 \pm 0.3$	$12.7 \pm 0.4$	$243.8 \pm 0.2$	$15.3 \pm 0.4$
K	$89.0 \pm 0.7$	$10.7 \pm 0.2$	$179.2 \pm 0.6$	$14.4 \pm 0.3$
K+L	$171.6\pm0.6$	$11.0 \pm 0.1$	$271.0\pm0.5$	$14.3 \pm 0.1$
L + K + L	$225.4 \pm 0.4$	$15.4 \pm 0.8$	$291.5 \pm 0.1$	$18.1 \pm 0.6$

#### 4. Discussion

There are a number of studies in the literature on the separate use of nano-SiO<sub>2</sub> and nano-TiO<sub>2</sub> materials in leather finishing. In a study by Ma et al., a composite of nano-SiO<sub>2</sub> and acrylic resin was used in the leather finishing operation<sup>6</sup>. It was found that the leathers finished with this composite developed dry rubbing fastness, bending strength and softness. Comparing our results with the results of this study, dry rubbing and bending strength values were found to be similar, while the wet rubbing value in our study was higher.

In other studies, a nano-SiO<sub>2</sub>/acrylic resin composite was used in the leather finishing process and it was reported that along with the increased values of dry rubbing, the finishing adhesion (9.38 N) increased by 10%<sup>7,27</sup>. However, the highest finishing adhesion values in our study were 11.1 N, showing an increase over the control samples of approximately 60%, and the wet rubbing fastness value was found to be higher (4/5-5) than the results of those studies (2/3-3).

It has already been reported that finish formulations incorporating silica sol-gel nanoparticles enhance the physical aesthetic and chemical properties of leather. The improvement obtained in covering, filling and other finish performance properties was due to the particle size which enhances the reactivity of SiO<sub>2</sub> nanoparticles with binders and other finishing auxiliaries<sup>27,28</sup>. Thus, we conclude that there is a chemical coalescence on the surface of the treated leathers between the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite and the lacquer used in finishing coating as it was determined by FTIR spectra and observed by SEM images.

In the previous reports on the use of a polyacrylate/ nano-SiO, composite, polyacrylate organosilicon and silica nanocomposite in leather finishing process it was stated that dry and wet rubbing fastness, the stretching strength, tearing strength and waterproofing of leather were improved<sup>29-31</sup>. In this way, it is clear that a finishing coat with the addition of nano-SiO<sub>2</sub> improves both the physical characteristics and the fastness values of leather. In our study it was observed that application of TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite by the 3<sup>rd</sup> variation (L+K+L) increased not only the wet and dry rub fastness properties of the leather but also color fastness to water and perspiration. At the same time, the finish adhesion and dry flex resistance of the leathers were improved. The last findings were supported with the results of the study in which with 9% hydrophobically and organically functionalized nano-SiO, particles in the finishing formulation, there was an increase of 25% in abrasion resistance, 20% in wet and dry rubbing fastness, 20% in rubbing fastness with alcohol, and 10% in flexing strength in the leather<sup>32</sup>. In our study the high rub-fastness and finish adhesion are primarily achieved by the crosslinking of the top coat1 since the high amounts of Si and Ti in the K+L+K leather samples determined by ICP-OES analysis.

Sudhahar et al. reported increasing the adhesion characteristic of leather by using nano-TiO<sub>2</sub> in leather coating<sup>33</sup>. The

researchers determined that TiO2 formed a stronger bond with the leather fibers by penetrating easily through the leather pores because of its nano size, and that it increased the intermolecular linkages between the finish coating and the leather surface. Bitlisli et al. investigated the effect of nano-TiO, in conferring the properties of self-cleaning and UV protection on finished leather<sup>5</sup>. The results of the study established that the resistance of the leathers to yellowing when exposed to UV light and the self-cleaning property increased. The best results were obtained when nano-TiO, was used in the top coat at a rate of 100%. In our study, it was observed that the TiO,-SiO, nanocomposite coating increased the color fastness values of the leather to light and UV light. It was thought that the presence of TiO, had enhanced the photocatalytic activity and that it was favorable in obtaining leather with improved color fastness to UV light.

In our study, we made use of the characteristics of both TiO<sub>2</sub> and SiO<sub>2</sub> materials in one composite, and it was established that leather finishing coating with TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite improved the physical and fastness characteristics of the treated leather samples.

#### 5. Conclusion

In this study, a technology was established to apply evenly distributed, smooth and homogeneous films of TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite to leather, especially in the third variation as L+K+L. Thus, performance qualities of the treated leathers such as dry and wet rubbing fastness, color fastness to perspiration and water, finishing adhesion and fastness to UV light, grain cracking and bursting resistance values were increased, benefitting from the qualities of the titanium and silicon dioxide compounds in the nanocomposite. It was concluded from the results obtained that nano-scale TiO<sub>2</sub>-SiO<sub>3</sub> composite could be used as a coating ingredient in the leather finishing process. Further studies are focusing on the introduction of the TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite in the base coat of a finishing formulation for industrial applications. Technology has forced leather manufacturers to move to the next level of leather quality, and leather customers also are demanding improvements in the performance characteristics of leather products. Therefore, it was intended in this study to make an innovative and useful contribution not only to the garment industry but also to the footwear and automobile industries, which are significant customers of the leather industry.

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