

APPLICATION OF TITANIUM METAL OXIDE NANOPARTICLES FOR LEATHER COATING

by

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ABSTRACT

Leather finishing is a very important operation in leather manufacture. Various chemicals are used in leather finishing. The introduction of nanoparticles in leather finishing has revolutionized the leather industry. They are used to produce various types of leathers and to meet the end user requirements. The aim of the work was to coalesce the fields of leather technology and nanotechnology for obtaining superior quality of leather with improved performance. Synthesis of titanium metal oxide nanoparticles was done by sol-gel process and used in leather finishing mixture as coating ingredients. The physical and chemical properties of the synthesized metal oxide nanoparticles were characterized by TEM, FE-SEM, EDAX, FT-IR and XRD. The surface morphology of the nanoparticle coated leather was evaluated by AFM. The finished leather was assessed for its film adhesion to evaluate the strength of the bonding between the leather surfaces and finish coating. The conventional finish system experience finish adhesion issue in due course of time. The titanium metal oxide nanoparticles coated leather exhibited increased adhesion property. TiO₂ nanoparticles increased the intermolecular linkages between the leather finish coating and the leather surface.

RESUMEN

El acabado del cuero es una operación muy importante en la fabricación de cuero. Varios productos químicos se utilizan en el acabado de cuero. La introducción de nanopartículas en el acabado de cuero ha revolucionado la industria del cuero. Se utilizan para producir diversos tipos de cueros y para satisfacer las necesidades de los usuarios finales. El objetivo de este trabajo fue unir los campos de la tecnología del cuero y la nanotecnología para la obtención de una calidad superior de cuero con un rendimiento mejorado. Síntesis de nanopartículas de óxidos metálicos de titanio preparados por proceso sol-gel y utilizado en la mezcla del acabado del cuero como ingredientes de recubrimiento. Las propiedades físicas y químicas de las nanopartículas sintetizadas de óxido de metal se caracterizaron por TEM, FE-SEM, EDAX, FT-IR y DRX. La morfología de la superficie del cuero recubierto con nanopartículas se evaluó mediante AFM. El cuero acabado se evaluó en su adhesión de la película y la fuerza de la unión entre las superficies de cuero y la capa de acabado. El sistema convencional acabado experimenta que la adhesión de acabado es cuestión de tiempo. El cuero acabado con nanopartículas de óxido de metal de titanio exhibió propiedades de adherencia aumentadas. Las nanopartículas de TiO₂ aumentaron las uniones intermoleculares entre el acabado y la superficie del cuero.

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INTRODUCTION

Leather is a by-product of meat industry. It is made from a natural hide or skin and becomes a non-putrefiable material after tanning, dyeing, fatiquoring, and finishing.¹ Leather has its special properties of viscoelastic behaviors, softness, fullness, roundness, strength, tightness, pliability, flexibility, stretch, adaptability and feel. Conventional leather finishing constituents were pigments, dye solutions, resin binders,² polyacrylate, polyurethane, waxes, fillers and nitro cellulose lacquers.³ We used TiO₂ metal oxide nano particles to enhance the performance of leather coating. Materials at nano sizes show special properties due to its aspect ratio i.e., large surface to volume ratio. Nano composites display novel properties due to strong chemical coalescent between the nanoparticles and polymer. TiO₂ metal oxide nano particles are used in wide range of applications such as anti fungal agent,⁴ super hydrophilic properties, water vapor permeability,⁵ solar cells,⁶ UV absorption,⁷ photovoltaic application,⁸ catalysis,⁹ semiconductor,¹⁰ plastics, fibers applications,¹¹ chromatography, controlled release, pigments,¹² optical hosts, electrical, thermal insulators, sensors,¹³ coating for adhesion, optical properties,¹⁴ electro chromic devices,¹⁵ self cleaning,¹⁶ gas sensors,¹⁷ scratch and abrasion resistance. The robust long life performance due to nano particles incorporated in leather coating helps the leather to last the test of time.

EXPERIMENTAL

Materials

Titanium Tetra Iso Propoxide (TTIP) was purchased from Sigma-Aldrich. Glacial Acetic Acid was purchased from SRL. Distilled water prepared in laboratory. Sarugan 919(PU Top) was purchased from Sarkem, Turkey. Akualene AKU (Cross linker) was purchased from Clariant.

Synthesis of Titanium Metal Oxide Nanoparticles

The TiO₂ nanoparticles were synthesized by sol-gel process. Titanium (IV) isopropoxide (TTIP) was used as precursor.^{18, 19, 28} TiO₂ synthesis process involves nucleation, gelation and ageing. It is a simple one step hydrolysis and condensation process, which involves the condensation of TTIP in water mixture at acidic condition at room temperature. The introduction of water into the system initiates hydrolysis in acidic solution.

TTIP, glacial acetic acid and water were maintained in the molar ratio 1:10:350. An experiment was carried out by taking 18.6 mL of TTIP in a 500 ml beaker, hydrolyzed by 35.8 mL of glacial acetic acid at 0°C. Then 395 mL of water was added slowly by drop wise in to the hydrolyzed mixture under vigorous stirring. It was stirred for 1 h followed by ultra sonication for 15 min. The stirring continued for further 1 h. The solution was prepared accordingly and kept for nucleation

process in the dark for 24 h. After that it was placed in hot air oven at 70°C for 12 h for gelation and ageing process. The gel was dried at 100°C and subsequently crushed into fine powder. It was annealed at 500°C for 5 h in a muffle furnace. This resulted in a fine white powder, which was characterized by FE-SEM, TEM, FT-IR and XRD and confirmed as nanoparticles of Titanium.

Preparation of Conventional Base Coat Finish Formulation, Incorporating TiO₂ Nano Particles, for Shoe Upper Leather

The synthesized TiO₂ nanoparticles were applied separately in shoe upper leather finishing formulation. It was used in base coat with various concentrations as per following Table I. Nano particle, dispersing agent and water were premixed and sonicated for 30 minutes and added to the coating mixture formulation i.e., with water, acrylic binder, polyurethane, casein, wax and pigment.^{20,21} Further the final mixture was sonicated for 30 minutes then sprayed on the cow shoe upper leather by HVLP gun at 30 psi. The base coat deposition was 8 g/sft applied by two cross coat spray, with intermediate drying. The dried leather was pressed at 80°C/80 kg/cm² then again two cross coat coating mixture was sprayed on the leather. After drying the leather was sprayed one cross coat of polyurethane top.

Topcoat Formulation

Sarugan 919 PU Top (Sarkem)	– 500 parts
Water	– 500 parts
Akualene AKU Cross linker (Clariant)	– 5parts (Cross linker pre mixed with water 5 parts)

The above formulation was sprayed one cross coat on leather by HVLP gun at 30 psi. Topcoat deposition was 4 g/ft². Then the leather was dried and pressed at 80°C/80 kg/cm².

RESULTS AND DISCUSSION

Structural and Morphological Characterization of TiO₂ Nanoparticles

Wide Angle-X-Ray Diffraction Spectroscopy (XRD) Analysis

X-ray diffraction analysis of TiO₂ nanoparticles were performed by RICHSEIFERT model 3000 diffraction system, Germany, with Cu K Alpha ($\lambda = 1.5405\text{\AA}$) radiation at 40 kV and 30 mA.

Figure 1 showed the WA-XRD diagram of TiO₂ nanoparticles. It shows well defined peaks corresponding to the TiO₂ nano particles. The 2 θ value of the sample was found to match with

TABLE I
Conventional base coat formulation incorporating titanium metal oxide nanoparticles for shoe upper leather.

Ingredients	Trial I	Trial II	Trial III	Trial IV	Control
Water	459.9	459.5	459	455	460
Primal 863 Acrylic resin	150	150	150	150	150
RU 3901 PU binder	150	150	150	150	150
Lustral UT Casein binder	50	50	50	50	50
SFT6004Wax emulsion	50	50	50	50	50
Pigment	125	125	125	125	125
Titanium metal oxide Nanoparticles*	0.1	0.5	1.0	2	0
Dispersing agent*	5	5	5	5	5
Water*	10	10	10	10	10

(*Nano particles, dispersing agent, water are premixed and sonicated. All the quantities given in the above table are in grams)

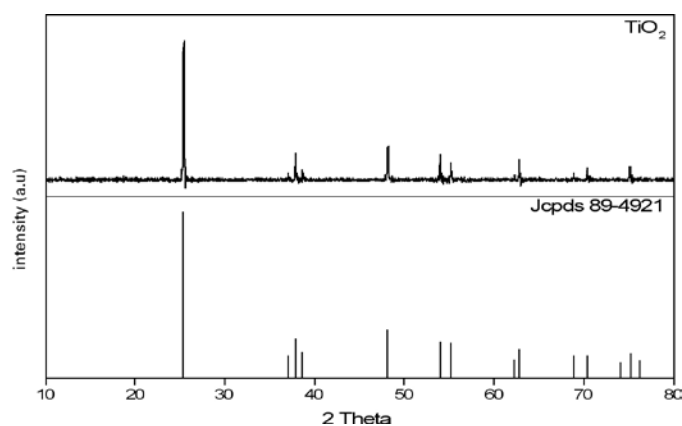


Figure 1. WA-XRD diagram of TiO_2 nanoparticles.

JCPDS file 89-4921. It confirms the size and lattice parameter as 43 nm and (101) plane. These values are in comparatively good agreement with the previous reports.^{18, 27, 28, 29, 30}

Field Emission Scanning Electron Microscope Imaging and Energy Dispersive Analysis

The formed titanium particles morphology was obtained from FE-SEM (HITACHI S-6600). Figure 2 showed the FE-SEM image of TiO_2 particles, which confirmed that it was in spherical shape with a string of beads like structure.^{22, 23}

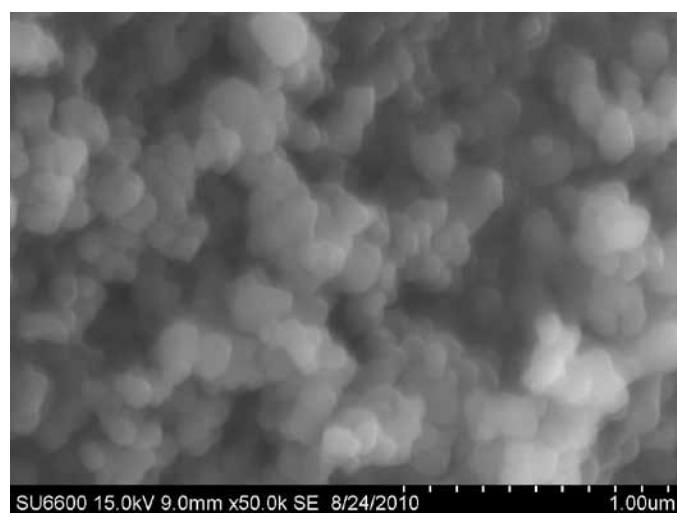


Figure 2. FE-SEM images of TiO_2 nanoparticles.

EDAX Peaks of Nano TiO_2 Powders

Figure 3 showed the EDAX results, which confirmed the presence of Ti and Oxygen elements, and the formation of TiO_2 particles.²²

Elemental Composition Analysis

Table II conferred the elemental composition analysis of titanium sol-gel nano particles. Atomic % of titanium was 26.78%.

TABLE II
Elemental composition analysis.

Element	Weight%	Atomic%
O K	47.73	73.22
Ti K	52.27	26.78
Totals	100.00	100.00

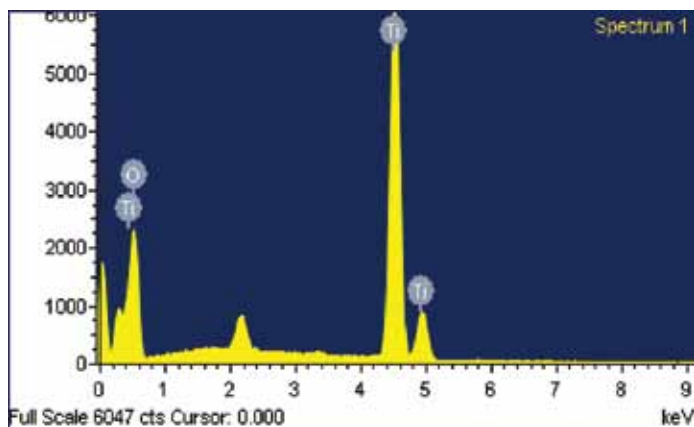


Figure 3. EDAX peaks of TiO₂ nanoparticles.

Atomic Force Microscope Image Analysis of TiO₂ Nanoparticles Coated Leather Sample

AFM was used to image and study the surface morphology of finished leather. Tapping mode AFM observations were performed by XE 100 from Park Systems in air environment. Single crystal silicon tips from Shocana were used and the force constant of the tip is 40 N/m. Figure 4 showed the topological image of crust leather. The troughs and crests were clearly visible in the 3 dimensional views. Figure 5 showed the topological image of control leather (with out TiO₂). The leather was finished by conventional base coat mixture. The surface morphology revealed that the leather was flat and smooth.²⁴ Figure 6 showed that the topological image of leather which was coated by TiO₂ nano particle in the base coat with the concentration of 2 g/KL in coating mixture. The image revealed that the nano particle was distributed uniformly.^{25,30} The existence of TiO₂ nano particles²⁸ in the coating film increases the adhesion of leather finish film with the surface of the leather, which is an important performance property for shoes.²

Determination of Applied Physical Properties for TiO₂ Nanoparticles Coated Leather

The following performance tests were carried out on the titanium sol-gel nanoparticles coated leathers.

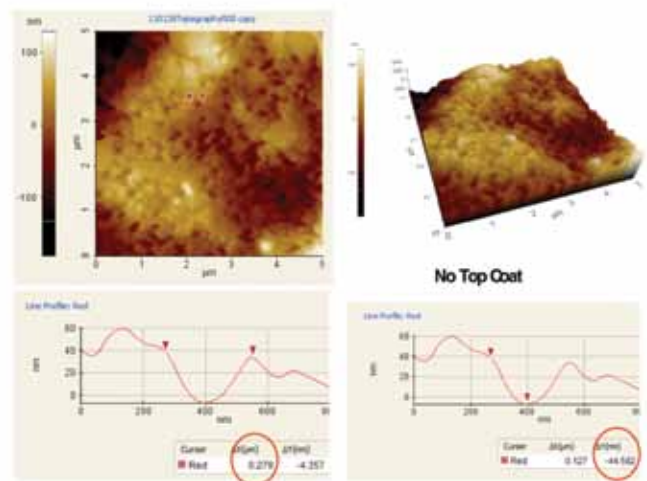


Figure 4. AFM image of Crust leather, 3 dimensional view.

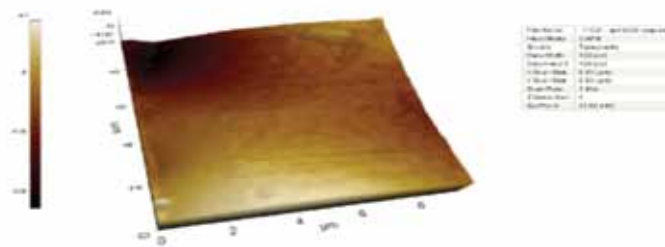


Figure 5. AFM image of Control leather, 3 dimensional view.

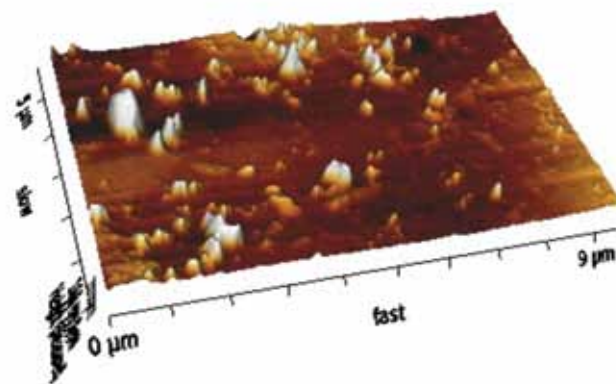


Figure 6. AFM image of TiO₂ coated leather.

Flexing Endurance

Measurement of Flexing Endurance test was carried out according to SATRA TM 55:1999. Type of machine used was Bally. The results are given in Table III.

Measurement of Finish Adhesion

Measurement of Finish Adhesion test was carried out by SATRA TM 416:1996. The values are given in Table III.

Performance Test Result for the TiO₂ Nano Particles Coated Leather

All the finished leathers were assessed for following physical and visual assessment parameters such as gloss, covering, tackiness, levelness, filling, feel, plate release, and fish-eye. The results are given in Table IV.

Subjective Evaluation Result for TiO₂ Nano Particles Coated Leather

The leather finish coat must adhere to the substrates to which it is applied. The improved adhesion properties were due to the presence of TiO₂ nanoparticles in leather finishes formulation. The greater surfaces to volume ratio (aspect ratio) of TiO₂ nanoparticles enhance the reactivity of binders and

other finishing auxiliaries with the leather substrate. When size reduces from bulk to nano scale, the electron density is greater, so the reactivity will be better and it will be faster as well. The surface forces are also involved in adhesion^{26,30}. The polar molecules of binders and TiO₂ are in contact. Sufficient intimate molecular contact is achieved at the interface for the materials to adhere due to inter-atomic and intermolecular forces³⁰. The relatively large fraction of surface atoms confers special properties to these materials, like increased adhesion, strength and enhanced diffusivity. Additionally, the extremely high surface area of nano scaled TiO₂ facilitated the adsorption of other finishing ingredients and enhances the reactivity.

TABLE III
Performance test result for the titanium metal oxide nanoparticles coated leather.

Performance Properties	Trial-I	Trial-II	Trial-III	Trial-IV	Control
Bally Flexing Dry 100,000	No crack	No crack	No crack	No crack	No crack
Finish Adhesion Test in N/10mm Dry	4.71	4.98	5.36	5.80	4.64
Finish Adhesion Test in N/10mm Wet	2.40	2.97	3.88	4.05	2.36

TABLE IV
Subjective evaluation result for titanium metal oxide nanoparticles coated leather.

Performance Properties of TiO ₂ coated leather	Trial-I	Trial-II	Trial-III	Trial-IV	Control
Gloss	4, Good	3 or 4, Medium to Good	3 or 4, Medium to Good	3 or 4, Medium to Good	4 or 5, Good to Excellent
Covering	2 or 3, Poor to Medium	3, Medium	3 or 4, Medium to Good	4, Good	2 or 3, Poor to Medium
Levelness	5, Excellent	5, Excellent	5, Excellent	5, Excellent	5, Excellent
Filling	3 or 4, Medium to Good	3 or 4, Medium to Good	3 or 4, Medium to Good	4, Good	3, Medium
Touch	3, Moderately Waxy & smooth	3, Moderately Waxy & smooth	3, Moderately Waxy & smooth	3, Moderately Waxy & smooth	2 or 3, Waxy & smooth
Tackiness	5, Fully Tack free	5, Fully Tack free	5, Fully Tack free	5, Fully Tack free	5, Fully Tack free
Fisheye	5, No fish eye	5, No fish eye	5, No fish eye	5, No fish eye	5, No fish eye
Plate Release	5, Very easy plate release	5, Very easy plate release	5, Very easy plate release	5, Very easy plate release	5, Very easy plate release

Rating description: 5-Excellent, 4- Good, 3-Medium, 2-Poor, 1- Very poor.

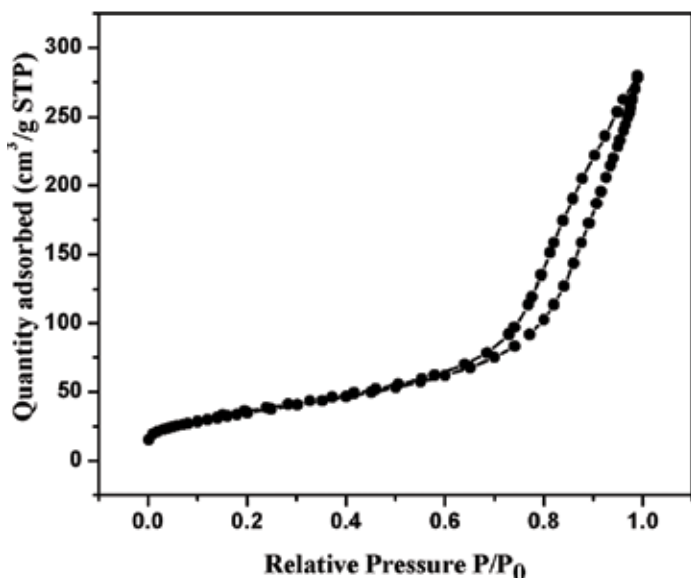


Figure 7. N_2 adsorption and desorption isotherm.

Figure 7 showed the typical N_2 adsorption and desorption isotherm. The particle surface area determined by using BET technique and it is measured that the specific surface area of $124.89 \text{ m}^2/\text{g}$ for the TiO_2 nanoparticles. Also, the TiO_2 nanoparticles are very small enough to penetrate in to the pores of the leather fibers and resulting in stronger interaction with leather fibers³¹. The existence of TiO_2 nanoparticles²⁸ in the coating film increases the adhesion of leather finish film with the surface of the leather, which is an important performance property for shoes². Excellent adhesion properties are already reported in textile coating application by using TiO_2 nanoparticles.³¹

CONCLUSION

The leather coated with TiO_2 nano particles exhibited an increased adhesion property. The improved adhesion property was due to the presence of TiO_2 nanoparticles in the leather finishes formulation. The greater surfaces to volume ratio (aspect ratio) of TiO_2 nano particles enhance the reactivity of binders and other finishing auxiliaries with the leather substrate. When size reduces from bulk to nano scale, the electron density is more, so the reactivity will be faster and better and it will be faster as well. The surface forces are also involved in adhesion. The polar molecules of binders and TiO_2 are in contact. Sufficient intimate molecular contact is achieved at the interface for the materials to adhere due to inter-atomic and intermolecular forces. The relatively large fraction of surface atoms confers special properties to these materials, like increased adhesion, strength and enhanced diffusivity. Additionally, the extremely high surface area of nano scaled TiO_2 facilitated the adsorption of other finishing ingredients and enhances the reactivity. Also the nano TiO_2

particles are small enough to enter in to the pores of the leather fibers and resulting in stronger interaction with leather fibers. Excellent adhesion properties are already reported in textile coating application by using TiO_2 nanoparticles. Finish adhesion test results were tabulated in Table III. All the leather samples treated using TiO_2 nano particles in finishing conferred finish film adhesion of 3 N/mm with no finish film peel off, meeting the standard shoe upper leather requirements.

The subjective evaluation results were given in Table IV. The leather samples treated with TiO_2 nano particle conferred medium gloss appearance but the control gave very high gloss. The value for control leather was 4 or 5 and Trial IV was 3 or 4 (2 g/L TiO_2 nano particle used).

TiO_2 nano particles incorporated finish formulations have enhanced the physical, aesthetic and chemical properties of leather. They conferred better covering, filling and settled appearance because of particle size, more surfaces to volume ratios enhancing the reactivity of binders and other finishing auxiliaries. The present study confirmed that the finish film adhesion (dry) was found optimum when the TiO_2 nano particle used in the range of 0.1 g/kL to 2 g/kL. TiO_2 nano particle coated leathers exhibited 25% increase in dry adhesion (2 g/kL) when compared to control (0 g/kL) tested. For wet adhesion (2 g/kL) there was 71% increase was observed when compared to control (0 g/kL).

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