

Zinc Oxide (ZnO) Nanoparticles for Enhancement of Fastness Properties in Cationic Finishing

by

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Abstract

Zinc oxide (ZnO) nanoparticles were synthesized by precipitation technique and used along with cationic finishes to improve the wet rub fastness properties and flexing resistance of coated leather. The morphology, composition, and structure of the ZnO nanoparticles were analyzed using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). ZnO nanoparticles were dispersed in water and incorporated in different ratios in conventional Nitrocellulose lacquer emulsion topcoat formulation was coated on the leather surface by spray coater. ZnO nanoparticles coated leather samples exhibited improved wet and dry rub fastness and flexing resistance property. Optimum quantity up to 2-4 g/L of ZnO nanoparticles in the season was desirable for upgrading the value of leathers. ZnO nanoparticles in cationic finishing can be highly beneficial for up gradation of low-grade crust with improved fastness properties without affecting its natural look and feel.

Introduction

Cationic finishing is widely used for the up gradation of low-grade crust leather without affecting the natural look. It imparts a well-filled look to leather while providing excellent coverage of defects. The main disadvantage in cationic finishing is its fastness properties do not match the performance of anionic finishing system. The recent development of the leather industry has increased the need for fine metal oxide particles with the application of nanotechnology like iron oxide (Fe_3O_4) nanoparticles have been selected for the enzymatic unhairing and fiber opening of skin,¹ bimetallic nanoparticles were used for the stabilization of collagen and as an eco-friendly tanning agent in the leather industry² for the manufacture of antibacterial leather and as a retaining agent by using ZnO nanoparticles.³ Moreover, nano-sized oxides (nano colorants) can be utilized as an excellent substitute to conventional toxic chemical like chromium, lead, and cadmium.⁴ Addition of inorganic

nanoparticles in leather processing helps leather to soften it by using nanoemulsions as retaining and lubricating agent⁵ and hydroxyapatite nanoparticles and polyethylene glycol to increase the softness and tensile strength of leather⁶ and incorporating nanoparticles in leather leads to enhancement of performance properties⁷ like adhesion strength (TiO_2),⁸ water spotting resistance, breathability (SiO_2),⁹ wet and rub fastness, color fastness to water and adhesion strength. (Cu).¹⁰ Zinc oxide (ZnO) has gained more attention because of its application in numerous fields such as in electronics,¹¹ optics,¹² photonics,¹³ varistors,¹⁴ photocatalysis,¹⁵ gas sensors,¹⁶ solar cells,¹⁷ pigments,¹⁸ etc. ZnO nanostructures were prepared by various methods such as laser ablation,¹⁹ hydrothermal methods,²⁰ electrochemical depositions,²¹ sol-gel method,²² chemical vapor deposition,²³ thermal decomposition,²⁴ combustion method,^{25,26} ultrasound,²⁷ microwave-assisted combustion method,²⁸ two-step mechanic chemical-thermal synthesis,²⁹ anodization,³⁰ co-precipitation³¹ and electrophoretic deposition.³² In this present study, ZnO nanoparticles have been synthesized by precipitation technique and incorporated into conventional leather finishing ingredients. Then the formulation was coated onto the leather by spray coating and evaluated for its organoleptic properties.

Experimental

Materials

Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and Sodium hydroxide (NaOH) were purchased from Merck (India), and deionized water was prepared in the laboratory. All the leather finishing chemicals were procured from TFL, Chrompet, Chennai, India and Stahl India. Pvt. Ltd, Nagalkeni, Chennai, India. Cow crust leather was obtained from Tannery Division, CSIR-CLRI, India.

Synthesis of ZnO Nanoparticles

To the aqueous solution of zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), the sodium hydroxide (NaOH) solution was added. The NaOH solution was added dropwise in a molar ratio

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of 1:2 under vigorous stirring. The stirring was continued for 12 h. and the obtained precipitate was filtered and washed several times thoroughly with deionized water. It was then allowed to air dried at 100°C and ground to a fine powder. The dried sample was then calcined at 800°C for 4h.

Preparation of Conventional Base Coat Leather Finishing Formulation

The cow upper base coat leather finishing formulation prepared as per Table I, i.e., with water, acrylic binder, PU resin binder, casein, filler, and the pigment was sprayed on the standard cow upper leather crust by HVLP gun at 30 psi. 8g/sft² was deposited on leather by two cross coat spray with intermediate drying.

Preparation of Top Coat Formulation with Incorporation of ZnO Nanoparticles

The synthesized ZnO nanoparticles were sonicated for 10 min and then they were incorporated in the top coat formulation with various concentrations for optimum results (Table II). The above formulation was sprayed by High Volume Low Pressure (HVLP)

Spray gun Bullows 630 at 30 psi. The formulation was deposited on the leather 4g/sft² by one cross coat. Then the leather was subjected to 80°C/80 kg/cm² pressure in a hydraulic press.

Results and Discussion

X-Ray Diffraction Spectroscopy (XRD) Analysis

Figure 1 shows the XRD image of ZnO nanoparticles. The diffraction peaks indicating the formation of pure ZnO nanoparticles are crystalline in nature. The peak intensity is sharp and narrow, confirming that the sample is of high quality with good crystallinity and fine grain size. The XRD pattern confirms the hexagonal ZnO wurtzite structure that is the predominant crystallographic structure according to the (JCPDS No. 89–0510). Typical XRD pattern of the hexagonal structure shows three strongest lines at 2θ values equal to 31.76°, 34.58° and 36.67° due to reflection from the crystallographic (100), (002), and (101) planes, respectively. The average crystallite size of ZnO nanoparticles was found to be equal to 43 nm.

Table I
Base coat formulations.

Sl.no	Ingredients	Parts	Percentage of solids	Characteristics of the product
1	Water	550	-	Aqueous
2	Resin binder RC 17787	150	(14.0-16.5)	Acrylic co-polymers cationic
3	PU binder RU 17702	100	18.0 – 21.0%	Aqueous aliphatic cationic polyurethane
4	Casein Melio K 201	50	5.5 – 6.5%	Formulated with water based cationic casein
5	Filler FI 1292	50	Ca.11	Aqueous cationic wax emulsion
6	Pigment PP 17724	100	30 – 32%	Water cationic pigment dispersion

(All the quantities given in the above table are in grams)

Table II
Top coat formulation with ZnO nanoparticles.

Sl.no	Ingredients	Control	Trial 1	Trial 2	Trial 3	Trial 4
1	ZnO NP's	0	1.25	2.50	3.75	5
2	LW-27-063NC lacquer	500	500	500	500	500
3	Water	500	498.75	497.50	496.25	495

(All the nanoparticles, water, and lacquer were used in grams)

Scanning Electron Microscopy (SEM)

Figure 2 shows the SEM image of ZnO nanoparticles. The morphology of the prepared nanoparticles was examined using scanning electron microscopy. Figure 2 shows that the surface morphology and shapes of the particles are nearly spherical and clearly shows a slight aggregation of the particles. The aggregation occurred probably during the process of drying.^{33,34}

Energy-dispersive X-ray (EDAX) Peaks of ZnO Nanoparticles

Figure 3 shows the EDAX results, which confirmed the existence of ZnO and Oxygen elements, and the formation of ZnO particles.

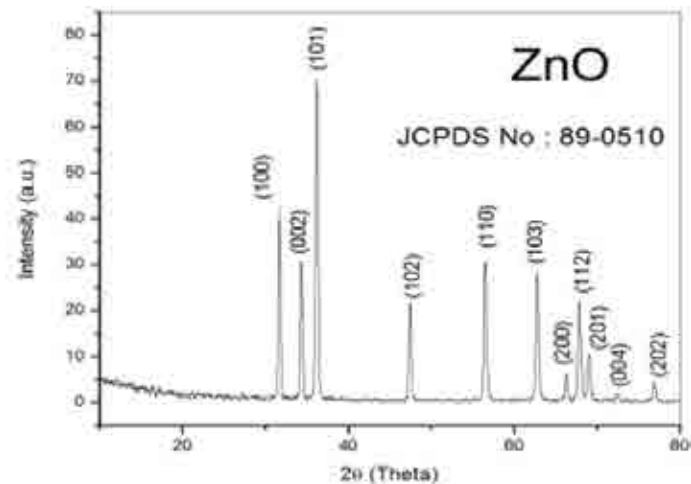


Figure 1. XRD diagram of ZnO nanoparticles.

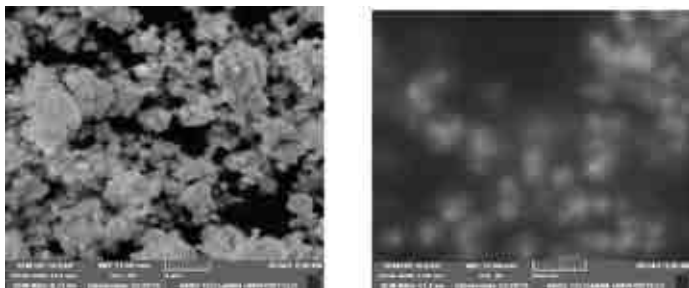


Figure 2. SEM images of ZnO nanoparticles.

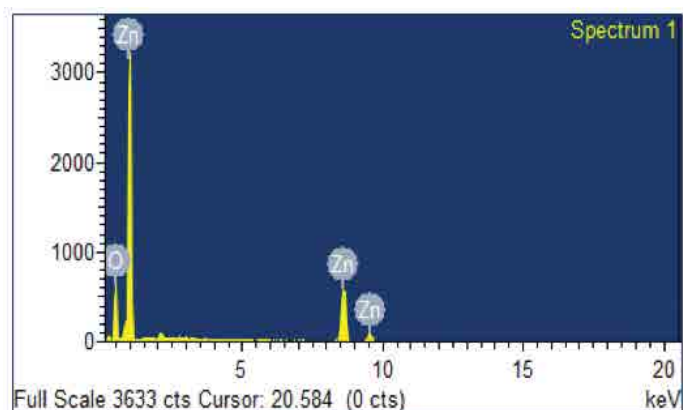


Figure 3. EDAX peaks of ZnO nanoparticles.

Elemental Composition Analysis

Table III conferred the elemental composition analysis of ZnO nanoparticles. Atomic % of Zinc was 42.37%.

Determination of Applied Physical Properties of ZnO Nanoparticles Coated Leather

The leathers, coated with ZnO nanoparticles, were evaluated for wet & dry rub fastness and flexing resistance properties which are tabulated in Table IV & V respectively.

Figure 4 shows the ZnO nanoparticles coated leather samples. The leather samples confer better filling and covering without affecting the natural look of the leather.

Wet and Dry Rub Analysis

Measurement of Wet and dry rub fastness test carried out according to IUF 450 by veslic C-4500, and the results were given in Table IV

Flexing Resistance

Measurement of Flexing resistance is carried out by SATRA STM 601/12 12, and the values given in Table V

Table III
EDAX peaks of ZnO nanoparticles.

Element	App Conc.	Intensity Corr.	Weight% Sigma	Weight%	Atomic%
O K	5.44	1.1113	0.82	24.97	57.63
Zn K	13.67	0.9296	0.82	75.03	42.37
Totals 100.00100.00					



Figure 4. ZnO nanoparticles coated leather samples.

Table IV
Wet and Dry rub fastness test result for the ZnO nanoparticles (on top coat) coated leather.

Sl.no	Rub fastness	Control	Trial 1	Trial 2	Trial 3	Trial 4
1	Dry	4	4	4	4	4
2	Wet	1	1	2	2	2

Table V
Flexing resistance test result for the ZnO nanoparticles (on top coat) coated leather.

Sl. no	No. of cycle	Control	Trial 1	Trial 2	Trial 3	Trial 4
1	10000	A	A	A	A	A
2	30000					
3	60000	B				
4	80000					
5	100000	E	C	B	B	C

*- Finished coat slight crack; A- No effect; B- Slight creasing; C-Slightly pipiness; D-Marked creasing; E-Severe creasing; F-Severe pipiness; H-Marked crack; I-Severe crack; J-Complete Failure

Figure 5 shows the of ZnO nanoparticles coated leather samples in dry and wet conditions after flexing resistance tests. Table V shows the Flexing resistance test result for the ZnO nanoparticles coated leather

Conclusion

The synthesis approach is simple and shows promising applications for the large-scale production of ZnO nanoparticles. The chemicals involved in the synthesis are commonly available, cost-effective, and non-toxic. This technology can be upscaled with minimum infrastructure and has the potential for commercial exploitation. XRD confirms the formation of ZnO nanoparticles at 36.67° (101) plane and using XRD data crystallite size was in the range of 43 nm. SEM image shows that the particles are in the spherical structure. EDAX investigates the stoichiometry and chemical purity of the samples to confirm the presence of Zinc and Oxygen. The present study establishes

that ZnO nanoparticles increase the wet rub fastness and flexing resistance properties. Optimum quantity up to 2-4 g/L of the ZnO nanoparticle is desirable for upgrading the value of leathers by improving wet & dry rub fastness and flexing resistance (in a wet condition) properties significantly.

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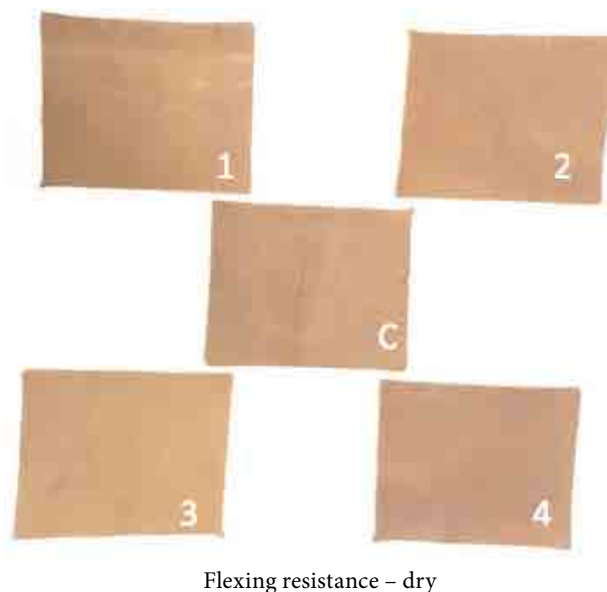
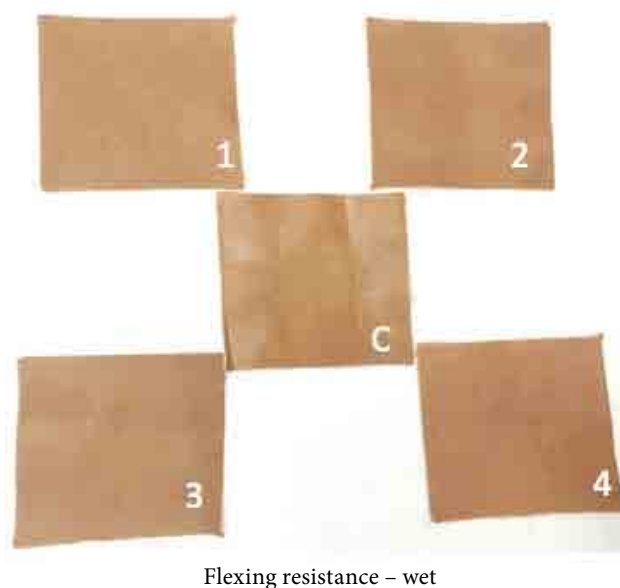


Figure 5. Flexing resistance (wet & dry) of ZnO nanoparticles.

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