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# Enhancing Performance Properties of Conventional Leather Finishing Topcoat by Incorporating Metal Oxide Based Formulations

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**Abstract.** ZnO nanoparticles were developed by 1:2 ratios of Zinc sulphate heptahydrate and Sodium hydroxide by using precipitation method. The structure, morphology of ZnO nanoparticles were investigated by using X-Ray Diffraction and Scanning Electron Microscopy. X-Ray Diffraction confirms the formation and average crystallite size of ZnO nanoparticles. Scanning Electron Microscopy studies shows the ZnO nanoparticles were in spherical in structure. ZnO nanoparticles were used in different ratios along with conventional finishing formulations and coated on the leather surface. The performance properties such as flexing resistance were evaluated. Application of ZnO nanoparticles in leather finishing showed significant improvement in overall performance properties than conventional finishing formulations. XRD confirms the formation of ZnO nanoparticles (wurtzite structure) at 36.31° (101) plane and the particles size was in the range of 34 nm. SEM image shows that the particles are in the spherical structure wheras EDAX investigate the stoichiometry and chemical purity of the samples to confirm the presence of zinc and oxygen. Optimum quantity up to 2-5 g/L of the season of ZnO nanoparticle is desirable for upgrading the value of leathers by improving the flexing resistance (wet & dry) properties significantly in PU top coat dispersions in finishing formulations.

## 1 Introduction

Leather finishing refers to the process of coating on leather surface to protect and beautify the leather i.e prolonging the lifetime of the leather, and considerably improving the quality and the commercial value of the leather products.(1,2) Conventional leather products lacks the appearance and performance properties required by the customer demands. Therefore, it is necessary to redesign and modify the conventional leather finishing formulations in order to achieve the improved organoleptic properties in leather finishing applications. Hence, much research work has been focussed on developing nanofinishing formulations to enhance the performance properties of the leather. Zinc oxide (ZnO) nanoparticles has gained more attention because of its application in numerous fields such as in electronics (3), optics (4), photonics (5), varistors (6), photocatalysis (7), gas sensors (8), solar cells (9), pigments (10) etc. In this present study, ZnO nanoparticles have been synthesized by precipitation technique

## 2 Experimental

### 2.1. Materials

Zinc sulfate heptahydrate (ZnSO4.7H2O) and Sodium hydroxide (NaOH) in analytical reagent grade were procured from Merck (India), and deionized water was used for the preparation of solutions. The cow crust leather was collected from Tannery Division, CLRI, India. All the leather finishing chemicals were procured from Stahl, Nagalkeni, Chennai, India.

### 2.2 Synthesis of ZnO nanoparticles

The aqueous solution of ZnSO4.7H2O and NaOH solution was prepared separately and added dropwise in a molar ratio of 1:2 under vigorous stirring, and the stirring was allowed to continue for 12 hrs.

The obtained precipitate was filtered and washed thoroughly with deionized water and followed by air drying at 100°C and ground to a fine powder. The obtained powder was calcined at 800°C for 4 hrs.

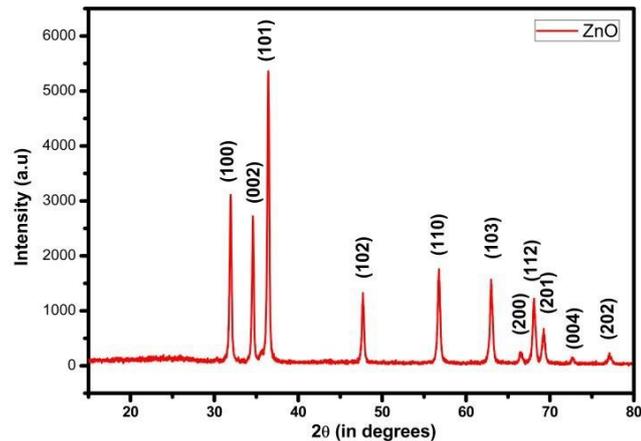## 3  Results and Discussion

### 3.1. XRD



**Fig. 1.** shows the XRD image of ZnO nanoparticles.

Figure 1 shows the XRD diffraction peaks of ZnO nanoparticles. The peaks indicating that the synthesized ZnO nanoparticles were crystalline in nature and the peak intensity is sharp and narrow which confirms the ZnO nanoparticles are in high quality with good crystallinity and fine grain size. The XRD pattern confirms the hexagonal ZnO wurtzite structure in the synthesized ZnO nanoparticles and in good agreement with the crystallographic structure (11) according to the (JPCDS card number: 36-1451). Typical XRD pattern of hexagonal structure of znO nanoparticles shows three strongest lines at $2\theta$ values equal to 31.82∘, 34.48∘, and 36.31∘ due to reflection from the crystallographic (100), (002), and (101) planes, respectively.
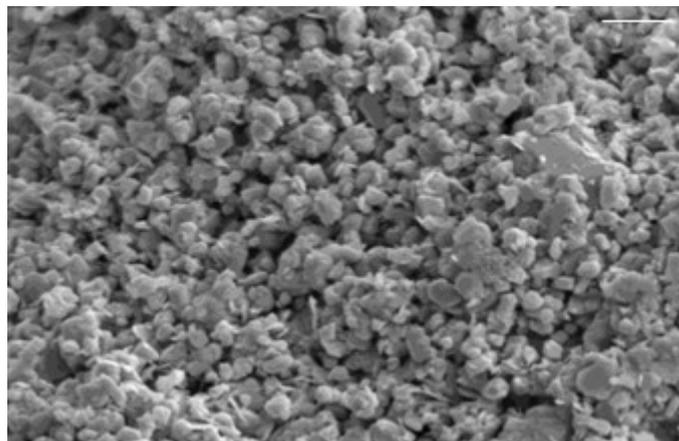
### 3.2 SEM



**Fig. 2.** shows the SEM image of ZnO nanoparticles.

The morphology of the synthesized ZnO nanoparticles was investigated by using scanning electron microscopy (SEM). Figure 2 shows that the surface morphology and shape of the ZnO nanoparticles are nearly spherical and agglomerated. The aggregation occurred probably during the process of drying [12,13].

## 4. Preparation of ZnO nanoformulations for leather finishing applications

Standard cow upper crust leather from Indian origin was selected for the evaluation. ZnO nanoformulations prepared for leather finishing applications carried out by leather PU top coat formulations and their performance properties were evaluated. A clearing coat (a mixture of ammonia, isopropyl alcohol (IPA) and water) were applied to increase the season adhesion with leather (Table 1). The cow upper base coat (Table 2) leather finishing formulation prepared 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. The formulation of 8g/sqft was deposited on leather by two cross coat spray with intermediate drying. The synthesized ZnO nanoparticles were sonicated for 10 min and then they were incorporated in the PU top coat dispersions (Table 3) in finishing formulation with various concentrations for optimum results. The above formulation was sprayed on by HVLP spray gun bullows 630 at 30 psi. The formulation was deposited on the leather 4g/sqft by one cross coat. Then the leather was subjected to 80oC/80 kg/cm2 pressure in a hydraulic press.

**Table 1.** shows the standard clear coat formulation.

| Sl. No | Ingredients | Mass (g) |
|--------|-------------|----------|
| 1 | Water | 470 |
| 2 | Ammonia | 5 |
| 3 | Isopropyl alcohol | 25 |

(All the values were expressed as g)

**Table 2.** shows the standard cow upper leather base coat formulation.

| Sl.No | Ingredients | Parts |
|-------|-------------|-------|
| 1 | Water | 550 |
| 2 | Acrylic resin | 150 |
| 3 | PU binder | 100 |
| 4 | Casein binder | 50 |
| 5 | Filler Wax | 50 |
| 6 | Pigment | 100 |

(All the values were expressed as g)

**Table 3.** shows the standard cow upper leather top coat formulation with ZnO Nanoparticles

| Sl.No | Ingredients | Control | Trial I | Trial II | Trial III | Trial IV |
|-------|-------------|---------|---------|----------|-----------|----------|
| 1 | Water | 500 | 498.75 | 497.50 | 496.25 | 495 |
| 2 | PU top coat | 500 | 500 | 500 | 500 | 500 |
| 3 | ZnO nanoparticles | 0 | 1.25 | 2.50 | 3.75 | 5 |

(All the values were expressed as g)

### 4.1 Determination of applied physical properties of ZnO nanoparticles coated leather

#### 4.1.1. Vamp Fluxing

Measurement of fluxing is carried out by SATRA STM 601/12 12 and the values are given in (Table 4).

**Table 4.** Performance properties of ZnO nanoparticles coated leather with PU top coat finishing formulations.

| Sl.No | Performance properties | Control | Trial I | Trial II | Trial III | Trial IV |
|---|---|---|---|---|---|---|
| 1 | **Flexing resistance (wet)** | | | | | |
| | **No. of cycle** | A | A | A | A | A |
| | 10000 | ↓ | ↓ | ↓ | ↓ | ↓ |
| | 30000 | ↓ | | | | |
| | 50000 | B | | | | |
| | 80000 | ↓ | ↓ | ↓ | ↓ | ↓ |
| | 100000 | C | B | B | B | B |
| | **Flexing resistance (dry)** | | | | | |
| | **No. of cycle** | A | A | A | A | A |
| | 10000 | ↓ | ↓ | ↓ | ↓ | ↓ |
| | 30000 | ↓ | | | | |
| | 50000 | B | | | | |
| | 80000 | ↓ | | | | |
| | 100000 | C | | | | |
| | 250000 | ↓ | | | | |
| | 300000 | ↓ | ↓ | ↓ | ↓ | ↓ |
| | 500000 | D | B | B | B | B |

*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.

## 5  Conclusion

ZnO nanoformulations were successfully prepared and its performance properties were evaluated. XRD confirms the formation of ZnO nanoparticles at 36.31o at (101) plane and using XRD data crystallite size is calculated as 30-70 nm. SEM image reveals that the particles are in nearly spherical structure and agglomerated. ZnO nanoparticles enhanced the flexing resistance properties along with conventional finishing formulations. Optimum quantity (upto 2-5 g/L in the season) of ZnO nanoparticle is desirable for upgrading the value of leathers.

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