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Fabrication of Printed Luminescent Finished Leather using Cu-doped ZnS: A Versatile and Luxurious Innovation

Md. Abdulla-Al-Mamun, Masrafe Bin Imran*

Institute of Leather Engineering and Technology, University of Dhaka, 44-50 Hazaribagh, Dhaka-1209, Bangladesh

ABSTRACT

This study introduces "Printed Luminescent Finished Leather," a novel finishing effect that enhances leather with a glowing feature. Copper-doped zinc sulfide (Cu-doped ZnS) luminescent pigment was synthesized via mixing and calcination at 600 °C, characterized by photoluminescent spectra (PL), X-ray diffraction (XRD), Fourier-transform infrared spectrometer (FT-IR), and Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) analysis. The analysis confirmed that Cu-successfully doped on ZnS nanostructure and exhibited Luminescent behaviour. Six leather samples, prepared with varying pigment quantities (3-7 gm/sq. ft), types (liquid and powder), and application methods (spraying, masking, stenciling, drop staining), and were evaluated through standard performance tests. These tests assessed color rub fastness, wash fastness, heat and perspiration resistance, with all samples scoring between 3 and 5 on the grey scale for finish film appearance and glow intensity under the both daylight and UV light. The adhesion strength of the finish film exceeded 200 gm/cm. The study found that a total luminescent pigment quantity of 7 gm/sq. ft yielded optimal results, with sample 5 exhibiting the best combination of glow intensity, adhesion, and persistence. The addition of luminescent pigments transforms ordinary leather into a visually appealing material, offering diverse applications such as fashion items, accessories, luxury upholstery, and interior design. This innovation holds significant economic potential for the leather sector, positioning it as a high-value product that can drive exports and satisfy consumer demands in global markets.

Keywords: Cu-ZnS nanocomposite, Phosphorescent materials, Leather finishing, Versatile leather, High-value product.

1. Introduction

The recent advancements in finishing significantly contribute to leather products becoming a fashionable part of our daily lives. The surface greatly influences the quality of leather products, affecting both the aesthetic appearance and the usable area of leather goods. Across numerous countries, leather finds extensive application in a myriad of sectors, ranging from the creation of leather goods and footwear to garments, accessories, jewelry, upholstery, and beyond.

The diversification of the leather industry presents a promising trajectory for the global market, positioning itself as a beacon of opportunity. This optimism is underpinned by the availability of abundant raw materials and an optimal environment conducive to the cultivation of high-quality rawhide and skin sourced from a variety of animals in the country such Bangladesh. This advantageous blend sets the stage for the cost-effective production of top-grade leather, requiring minimal effort to achieve excellence. As a result, the industry stands poised to make significant contributions to the market, fueled by its ability to provide top-quality leather products efficiently and sustainably.

Distinguished on the global stage, Bangladesh has earned acclaim as one of the foremost leather exporters worldwide. The country's robust leather industry extends its influence across various sectors, prominently featuring the export of leather products, footwear, apparel, garments, and an array of other goods. As a results, the leather industry has emerged as a key contributor to Bangladesh's export earnings and plays a pivotal role in generating employment opportunities [1].

Amidst a wealth of opportunities, innovations hold the potential to significantly enhance the economic standing and export prowess of the leather industry, akin to the strides made by the garments and textile sectors. In alignment with this perspective, our focus has shifted towards refining and modernizing conventional leather finishing techniques, giving rise to the "Printed Luminescent Finishing of Leather" study. This pioneering endeavor aims to imbue leather with a unique luminosity, allowing it to glow both day and night.

Luminescent leather, characterized by its capacity to emit light in the dark, is a product of treating or covering leather with luminous elements such as phosphorescent or fluorescent dyes. These materials absorb light energy and subsequently release it, resulting in a captivating and visible glowing effect. It is noteworthy that the luminous quality in leather is typically achieved through specific coatings or luminescent pigments, rather than being an inherent attribute of the leather itself.

In particular, for the leather coating, our approach draws inspiration from the captivating mechanism observed in fireflies that emit a luminous glow in the dark, aiming to enhance the aesthetic appeal of leather goods. By incorporating metal/metal ion-doped/oxide/sulphide luminescent materials composed of nanoparticles within a coating matrix, the surface structure necessary for the mesmerizing "Firefly-Effect." The chemical bonding established between the nanoparticles and the leather surface not only imparts a vivid blue glow but also ensures durability and high-performance diverse applications.

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*Corresponding Author Email Address: mamun.ilet@du.ac.bd

The present study is to address the research gaps in conventional leather manufacturing finishing processes, including the use of photocatalysts, metal/oxide nanoparticle, and luminating nanomaterials applied at various stages of leather manufacturing to achieve better performance. The manufacturing and fabrication processes also need to be environmentally friendly, low-cost, and more efficient compared to commercial one.

2. Experimental

2.1 Synthesis of luminescent Cu-doped ZnS nanocomposites

The mortar and pestle method, also known as the solid-state reaction or mechanical mixing technique, is a simple and cost-effective approach for doping materials. For instance, doping copper into zinc sulfide (ZnS) using this method involves accurately weighing the required amounts of ZnS powder and copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$] based on the desired doping concentration.

Add the ZnS powder and the copper source to the mortar, ensuring their proportions are determined according to the intended doping level. For example, if $Cu(NO_3)_2 \cdot 3H_2O$ is used as the dopant, combine it with ZnS powder in the correct stoichiometric ratio.

Employ a pestle to thoroughly grind the mixture in the mortar, facilitating uniform blending and ensuring the dopant is evenly distributed throughout the ZnS matrix. The grinding process typically requires 8 to 12 hours of continuous effort to achieve a fine and consistent mixture. If needed, ethanol or acetone can be added to aid the grinding process and improve homogeneity.

If wet grinding is employed, allow the solvent to evaporate by drying the mixture at room temperature or under slightly elevated temperatures. Ensure the mixture is thoroughly dried before moving on to the next step.

To ensure uniform particle size, the mixture can be passed through a sieve. This process helps achieve a consistent particle size distribution in the doped ZnS powder, which is essential for certain applications.

To facilitate the diffusion of dopant ions into the ZnS lattice, the doped mixture can undergo calcination. This involves heating the mixture in a furnace at a suitable temperature, typically ranging from 500 to 800 °C, for a designated period, such as 2 to 4 hours.

The calcination temperature and duration are determined by the thermal stability of the materials and the required level of dopant diffusion. After calcination, allow the doped ZnS powder to cool to room temperature. Once cooled, collect the powder and store it in a dry, airtight container to avoid contamination and moisture absorption.

2.2 Characterizations of luminescent

The synthesized Cu-doped ZnS samples were subjected to photoluminescence analysis using a UV-visible photoluminescence spectrophotometer (Biobase, BK-F96S) with the excitation wavelength of 320 nm. The functional groups and potential chemical interactions within the composites were characterized using Fourier-transform infrared spectroscopy (FT-IR, Bruker, Alpha II), which recorded spectra in the wavenumber range of 4000-400 cm^{-1}, with a resolution of 4 cm^{-1} and 30 scans. Crystallographic properties and diffraction patterns were determined using an X-ray diffractometer (Ultima IV, Rigaku Corporation, Akishima, Japan) equipped with Cu Kα radiation ($\lambda = 0.154$ nm), at a scanning rate of 0.30°/min over a 2θ range of 10°-80°. Thermogravimetric analysis (TGA) was carried out using a PerkinElmer TGA 8000 analyzer. The surface morphology of the samples was observed through Scanning Electron Microscopy (SEM) using a JSM-7610F (JEOL, Japan). An energy-dispersive X-ray spectrometer (EDX) was also utilized for the elemental analysis.

2.3 Methodology of leather luminescent coating

6 pieces of wet blue was taken and white crust is prepared based on chrome-alum combination tanning method and used special white syntan. Avoided aldehyde for yellowish effect. Three different methods have been used to impart design on different leather sample. They are: (a) *Spraying* (b) *Painting with stencil and paint brush* (c) *Drop staining using feather* shows in flow chat in Fig.1.

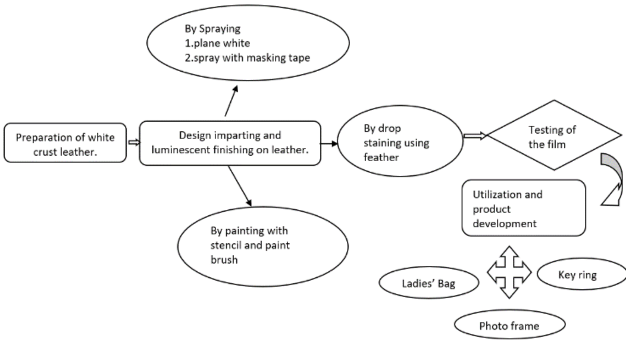


Fig.1 Experimental flowchart of luminescent finished on leather surface.

2.4 Test of finish film

Several tests for finish film were performed. They are:
Finish Film Adhesion Test (SATRA AM 08)
Color rub fastness test (Dry and wet) (SATRA PM 08)
Wash fastness test (soap, detergent and alcohol)
Perspiration resistance test (BS EN ISO 105)
Resistance to Aldehyde vapor test (IUF 424)
Heat resistance test (SATRA PM 49)

All the test carried out under standardized methods. sample size, equipment's and machineries, time duration and procedures were followed according to the methods for leather finish film testing [2-7].

3. Results and discussion

3.1 Photoluminescence spectra analysis

Fig. 2 presents the luminescence peak curves of pure ZnS and Cu-doped ZnS nanoparticles. The emission band of pure ZnS nanoparticles is observed at 375 nm.

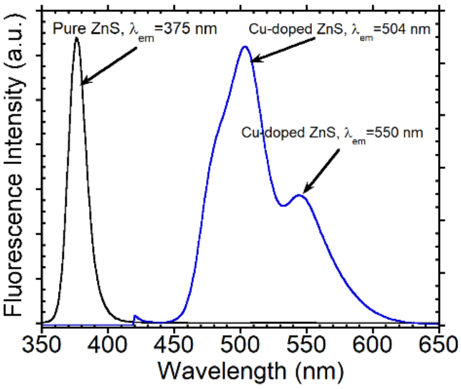


Fig.2 Luminescence spectra of bare ZnS and Cu-doped ZnS nanoparticles.

In the case of Cu-doped ZnS nanocrystals, two distinct emission bands are evident: one at 504 nm (blue band) and another at 550 nm (green band). Upon doping with Cu, the emission wavelength extends to lower energy levels, with emission centered between 500 and 550 nm. The emission spectra of Cu-doped ZnS nanoparticles differ significantly from their undoped counterparts. Based on the symmetry of the spectra, it is believed that the emission band arises from the doped-nanoparticles luminescence centers of Cu within the ZnS nanocrystals. Moreover, the relative fluorescence intensities of the Cu-doped samples are significantly enhanced.

3.2 XRD analysis

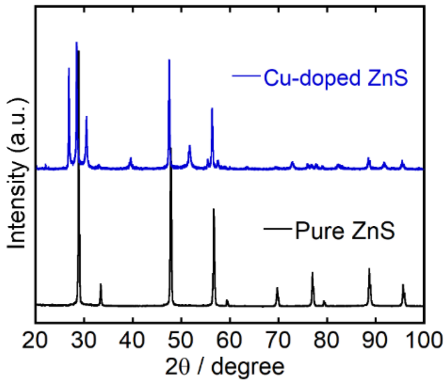


Fig.3 The powder X-ray diffraction pattern of pure ZnS and Cu-doped Zns, confirming the formation of pure metallic incorporate with copper-ZnS nanoparticles.

Fig. 3 presents the XRD patterns of the prepared ZnS and Cu-doped ZnS nanoparticles. The observed peaks correspond to specific crystallographic planes. Compared to pure ZnS, the Cu-doped ZnS nanoparticles exhibit additional peaks at 2θ = 26.884°, 30.375°, 39.59°, 51.75°, and 91.72°, which can be attributed to the diffraction of the (111), (200), (220), (311), and (222) planes of polycrystalline copper (JCPDS, PDF File No. 00-001-1241). The peaks for pure ZnS align with the reference pattern (JCPDS, PDF File No. 03-065-9585), confirming the formation of intrinsic Cu in the doped ZnS structure.

3.3 FTIR analysis

Fig.4 presents the FTIR spectra of ZnS nanoparticles and Cu-doped ZnS in the range of 4000–500 cm⁻¹.

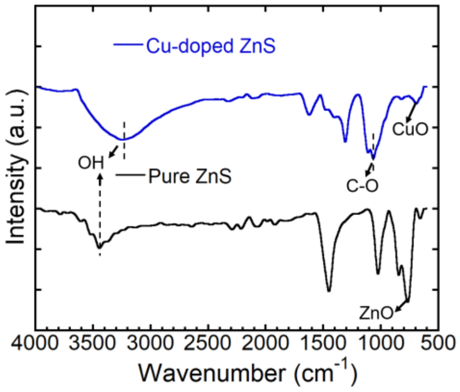


Fig.4 FTIR spectra of pure ZnS and Cu-doped ZnS nanoparticles.

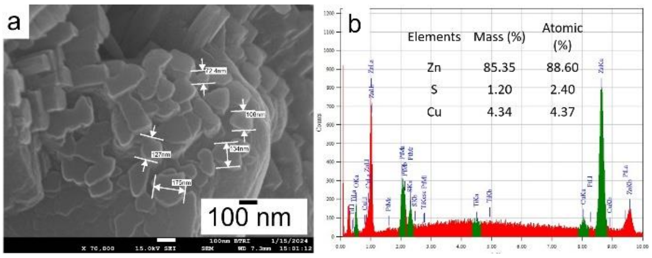
The peak at 626 cm^{-1} corresponds to the O-H bending of the hydroxyl group, while a broad absorption band in the 3400-3460 cm^{-1} range is attributed to O-H vibrations. Notably, the broad peaks around 3455 cm^{-1} and 1146 cm^{-1} are linked to O-H stretching in the Cu-Zn-O lattice. After doping ZnS nanoparticles with copper, a reduction in the intensity of the O-H absorption band indicates a decrease in the surface concentration of hydroxyl groups.

The peak at 1034 cm^{-1} corresponds to C-O, while absorptions at 835 cm^{-1} and 626 cm^{-1} are attributed to Zn-O stretching. The appearance of a band at 656 cm^{-1} is assigned to Cu-O stretching, confirming the incorporation of copper. The FTIR analysis confirms that Cu atoms have been substituted into the ZnS lattice, synthesized via the mixing process.

3.4 SEM and EDX analysis

The surface morphology of Cu-doped ZnS nanoparticles is presented in Fig. 5a. The SEM images clearly reveal that the average size of the nanoparticles is in the nanometer range. The Cu-doped ZnS nanoparticles (Fig. 5a) exhibit a homogeneous structure, with particles uniformly distributed across the surface and demonstrating good connectivity. The particles consist of a mixture of spheroid-like and rod-like shapes, with spheroid-like particles being predominant, and grain sizes measuring less than 100 nm.

Fig. 5b shows the EDXS spectra, confirming the presence of Zn, S, and Cu in the nanoparticles. The atomic ratio of Zn, S, and Cu is 88:2:4, closely matching the expected stoichiometry. Some impurities were also detected within the sensitivity range of the EDXS. Additionally, the Pt peaks observed in the spectra are attributed to the Pt-SEM grid used as a background.



Elements	Mass (%)	Atomic (%)
Zn	85.35	88.60
S	1.20	2.40
Cu	4.34	4.37

Fig.5 (a) Scanning electron microscope (SEM) pictures and (b) Energy-dispersive analysis X-ray (EDAX) pictures of Cu-doped ZnS nanoparticles annealed at 600 °C.

3.5 Utilization of Cu-Doped Luminescent Materials in Leather Surface Finishing for Product Development

By Spraying (Three samples)

Plane white (sample1 and sample2): Two different white crust leathers were finished using the simple method illustrated in Fig. 6. The key difference between the samples was the amount of fluorescent pigment used. Both leathers were initially given a white base coat using a standard hand-spray finishing technique. Subsequently, the intermediate and top coats were applied.

Spray with masking tape (Sample3): Two cross-coatings were sprayed onto the leather surface to create a white base coat. After drying, masking tape was applied to the leather surface, followed by plating at 80 °C and 35 bar, as shown in Fig. 6. A contrasting intermediate layer, using black pigment, was then applied. The masking tape was removed after the layer had dried.

A stencil with a predetermined design was created using plastic paper, as shown in Fig. 7. The base coat and all subsequent layers were applied in the same manner as in Sample 3. However, the key difference in this process is that the intermediate design contrast was created by placing the stencil on the leather after applying the base coat and intermediate coat. The black color contrast was manually applied using a paintbrush. Notably, the amount of luminescent pigment used was the same as in Sample 3.

This process is very similar to that of Sample 3 and Sample 4. The key difference is that the drop stain contrast was achieved by randomly applying splashes of multicolored pigments (red and blue) using 3 or 4 chicken feathers, as shown in Fig. 8. This step was performed manually. Another important variation is the differing quantities of luminescent pigment used in intermediate coat and the top coat. Additionally, the distinction between Sample 5 and Sample 6 lies in both the quantity and type of luminescent pigment applied. The final appearance of all six printed luminescent leather swatches is shown in Fig. 9.

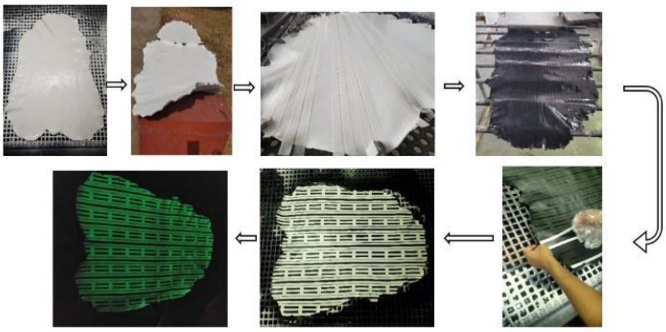


Fig.6 Steps of design imparting by masking tape

By painting with stencil and paint brush (sample 4)

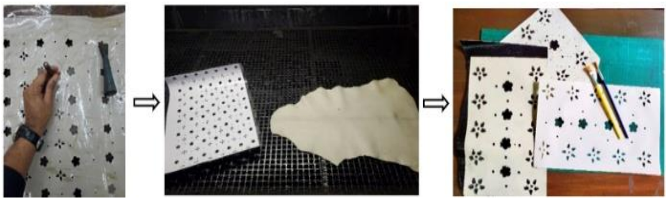


Fig.7 Steps of design imparting by stencil

By drop staining using feather (Sample 5 and sample 6)

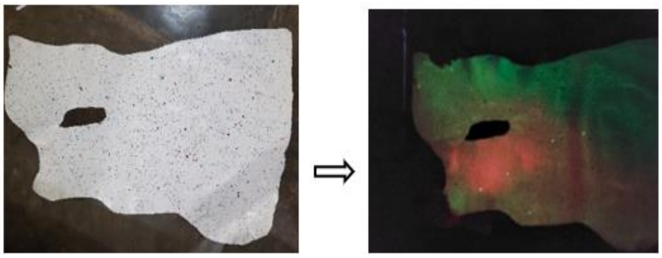


Fig.8 Design imparting by drop staining

Fig.9 Final appearance of all six printed luminescent leather swatch

3.6 Sequential operation for manufacturing Ladies Bag

The first step involved designing the bag and developing the pattern based on the design (Fig. 10, left). The subsequent steps included material cutting, sewing, assembling, and finishing, which involved removing excess adhesive, burning loose threads, and cleaning off dust. The final product, including a day and night view, is shown in Fig. 10 (right).

Fig.10 Ladies bag pattern (left) and final view of ladies' bag at day and night (right).

3.7 Sequential operation for manufacturing photo frame

A design was selected for the shape of the leather. The next step involved developing all the necessary patterns (Fig. 11). All the steps required for manufacturing the photo frame were then carried out successively. The final view of the photo frame, including both day (left) and night (right) views, is shown in Fig. 11.

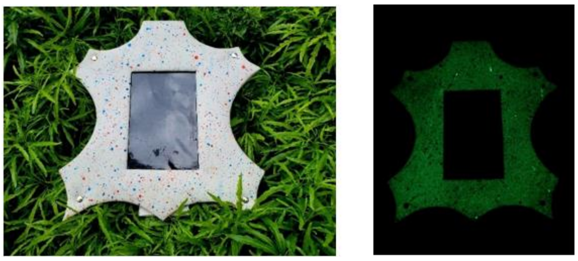


Fig.11 Photo frame (Day and night view)

3.8 Sequential operation for manufacturing Key Ring

The process began with the careful selection of raw materials, tools, and machinery, followed by pattern making (Fig. 12). As with the previous products (ladies' bag and photo frame), the steps of material cutting, sewing, and assembling were carried out systematically. The finishing process involved refining the product by removing excess adhesive, trimming any loose threads, and ensuring a clean and polished appearance. Each step was executed in a sequential manner to ensure precision and quality. The final product is displayed in Fig. 12.

Fig. 12 Key ring pattern (left) and final view of key ring at day and night (right).

3.9 Finish film adhesion test

The results of the finish film adhesion test for all six samples are presented in the Table 1 below, highlighting the adhesion strength and overall performance of each sample.

Table 1 Finish film adhesion test results of all six samples.

Sample number	Load required (gm/cm)	Standard (gm/cm)	Ref.
Sample 1	450	Minimum 200	[2]-[7]
Sample 2	450		″
Sample 3	350		″
Sample 4	350		″
Sample 5	650		〃
Sample 6	700		〃

The results from the adhesion test reveal that all six samples performed exceptionally well. The standard minimum value for this test is 200 gm/cm; however, in this case, the lowest recorded load was 350 gm/cm, observed in Sample 3 and Sample 4. This could be attributed to the heavily loaded top coat containing solid luminescent particles, which may have contributed to a slightly lower performance. On the other hand, Sample 6 and Sample 7 produced particularly impressive results. This may be due to the lower use of luminescent pigment in the top coat and a higher load of binder in the intermediate layers. Sample 6 stood out as the top performer, likely because of the minimal use of solid pigments combined with liquid luminescent pigments. The use of liquid pigment did not compromise the film’s strength, allowing it to maintain superior adhesion.

3.10 Color rub fastness test

The color rub fastness test results (dry and wet) for all six samples are provided in Table 2 below.

Table 2 Color rub fastness (dry and wet) test results of all six samples. Rating by gray scale.

Sample number	Dry condition (after 1024 cycles)		Wet condition (after 512 cycles)	
	Day light	UV light	Day light	UV light
Sample1	5	5	4/5	4
Sample2	5	5	4/5	4
Sample3	5	5	4/5	4/5
Sample4	5	5	4/5	4/5
Sample5	5	5	5	5
Sample6	5	5	5	5

The results from the color rub fastness test show that all six samples performed exceptionally well, maintaining their impressive performance from previous tests. The standard acceptable rating for this test is between 3 and 5 on the gray scale. In this case, the lowest rating observed was 4/5 under wet conditions, found in Sample 3 and Sample 4. However, under dry conditions, all samples achieved the highest possible rating. Furthermore, the UV light exposure test showed only minimal variation, indicating that the fixation of luminescent particles was very strong. These results confirm that the color rub fastness of all the samples is well within the standard threshold, demonstrating excellent durability in both wet and dry conditions.

3.11 Wash fastness test

The wash fastness results, as shown in Table 3, demonstrate outstanding performance, with all samples achieving a perfect gray scale rating of 5 out of 5. This indicates excellent resistance to color fading or alteration after washing, further emphasizing the durability and quality of the samples.

Table 3 Wash fastness (soap and detergent) test results of all six samples. Rating by gray scale.

Sample name	Soap fastness		Detergent fastness	
	Leather	Fabrics	Leather	Fabrics
Sample 1	5	5	5	5
Sample 2	5	5	5	5
Sample 3	5	5	5	5
Sample 4	5	5	5	5
Sample 5	5	5	5	5
Sample 6	5	5	5	5

Based on the test results, it can be concluded that the glow intensity of luminescent finished leather increases linearly with the amount of luminescent pigment applied. However, exceeding the optimal quantity-determined to be 7 gm/sq. ft-may lead to a decrease in adhesion strength, resulting in reduced rub fastness, film cracking, and other issues. Another important finding is that the maximum amount of pigment should be applied to the intermediate layer rather than the top layer. Although higher pigment usage increases the glow (as observed in sample 3 and sample 4), it should be avoided due to durability concerns. The finishing technique applied in sample 5 is the most optimal, offering a standard approach for achieving both aesthetic and functional efficiency.

4. Conclusions

The luminous finishing experiment on leather represents a significant advancement in the leather industry, offering promising results for enhancing leather aesthetics. The study goal of exploring new techniques to make leather products more visually appealing has been successfully demonstrated through the introduction of luminous particles via a manual hand spray method. This innovation paves the way for the creation of unique, eye-catching leather goods that cater to modern consumer demands in sectors such as fashion, accessories, and interior design.

The addition of luminosity to leather goods presents a unique visual effect, offering customization potential that could attract a wide range of customers. As research progresses, the luminous effect can be refined to create diverse patterns, designs, and color combinations, appealing to consumers who value individuality and style.

The market for luminous leather products is expected to expand, especially among fashion-conscious consumers, luxury buyers, and interior designers. This modernized take on traditional leather offers a blend of classic elegance and contemporary innovation, which is likely to increase demand. Early adopters of this technology stand to benefit from a competitive edge, with opportunities for higher profits due to the premium pricing of luminous leather items.

In conclusion, the successful luminous finishing experiment marks a milestone in leather industry innovation. By meeting the evolving preferences of today's consumers, luminescent leather products hold the potential to become a lucrative market segment, driving both growth and innovation in the industry.

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