THE EFFECTS OF DIFFERENT LACQUERS USED IN FINISHING ON LEATHER COLOR CHANGE

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Although there are many factors affecting the final color of the leather, it is wondered whether it has a significant contribution since final coat is the last step for the production of leather in finishing. It is necessary to determine which lacquer emulsion or emulsions are causing this situation, which may result in cost, time, and quality losses. For this reason, in this study, firstly, three different lacquer emulsions, namely Nitrocellulose, Cellulose Aceto Butyrate and Polyurethane, were applied to the leathers dyed with the same finishing composite (base coat) at the final stage. These lacquer emulsions are widely used in leather finishing. Water-soluble forms of these materials, including solvent-soluble types, were chosen for use in this study because they are more environmentally friendly and easier to apply. After that, leather colors were analyzed for color parameters determination by using Konica Minolta brand CM 3600d Spectrophotometer and compared with the color changes before and after the lacquers were applied. Finally, The NCSS (Number Cruncher Statistical System) 2022 Statistical Software (NCSS LLC, Kaysville, Utah, USA) program was used to statistically evaluate the results. As a result, it was attempted to identify the lacquer emulsions that causes the color change in the leather.

Keywords: finishing, laquer, color change

INTRODUCTION

The finishing process, which is the final stage of the leather production process in tanneries, is critical in ensuring that the final product has the appropriate resistance properties. Finishing enhances the appearance of leather by reducing surface defects and scratches, providing shine, feel, color match, color effects, and aiding in the preservation of the leather's natural appearance (Winter *et al*., 2015).

Three foundation coats - Base Coat, Pigment Coat, and TopCoat - make up finishing (Sasikala *et al*., 2007). The surface characteristics of the leathers are chemically altered to fix the finishing chemicals in the base coat. The leathers are given a uniform color by the pigment coat. To enhance physical qualities, fillers and binders are additionally utilized. To protect the leather finish, topcoat is made up of lacquers based on polyurethane and cellulose derivatives (Tamilselvi *et al*., 2019). Topcoat can provide leather excellent fastness and mechanical qualities because it is reasonably hard and more abrasion-resistant (Wu *et al*., 2021). The final appearance and texture of the leather surface are determined by the finish. Additionally, it has a considerable impact on the finished leather's fastness qualities. Nowadays, there is an increasing preference for water-based topcoat systems over organic, solvent-containing varnishes and topcoats (Dix and Kirchner, 2002).

Isocyanates, polyols, and/or NH-functional chemicals are combined to form polyurethanes (Dix and Kirchner, 2002). To guarantee the leather has strong light fastness, the top coating is made of solvent-based aliphatic polyurethanes (PU). Solvent-based PUs are nevertheless prohibited because of their toxicity and environmental issues. The creation of water-based polyurethane (WPU) has shown to be a successful method for reducing organic solvent emissions significantly. In most cases, hydrophilic alteration is necessary for PU to dissolve in water. WPU can be classified into three groups based on the hydrophilic elements that make up the PU backbone: anionic

https://doi.org/10.24264/icams-2022.III.7

(carboxylic ion), cationic (ammonium ion), and nonionic (polyethylene glycol). The most popular water-based leather finishing material among them is anionic WPU because of its excellent dispersion stability and ease of mass manufacture (Wu *et al*., 2021).

By processing cellulose with a solution of nitric and sulfuric acids, nitrocellulose (NC) is created. The cellulose's hydroxyl groups (OH) are changed to nitrate groups (NO3) during this process, improving its ability to dissolve in solvents and transforming it into a transparent lacquer. Solvent-based NC lacquer, when applied as a topcoat, can enhance leather in a number of ways, including superior water resistance, good dry and wet friction fastness, filth resistance, and resistance to mechanical stress. Its distinctive high shine feature can be utilized for leathercraft, shoes, and other items. It enhances the value and beauty of leather, making it desirable in leather goods. To lessen the concerns that volatile organic compound (VOC) emissions pose to the environment and human health, water-based NC polish emulsions have recently been created. There are generally three ways to make aqueous NC dispersions. One involves emulsifying NC with the addition of surfactants. First, NC is dissolved in small volumes of organic solvents. Next, the NC solution is emulsified in water using surfactants, and the water-based product is produced by vacuum distillation after the organic agents have been removed. Phase inversion is the second strategy. The surfactant solvent combinations are used to first emulsify the NC, and then water is added while being vigorously stirred. These results in the transformation of the water-in-oil (W/O) emulsion created in the initial stage into an oil-in-water (O/W) emulsion. The third method is self-emulsification, which involves covalently immobilizing hydrophilic groups within the NC to increase its hydrophilicity and aid in its dispersion in water (Wu *et al*., 2021). Nitrocellulose emulsions give the leather a natural feel. It flows well and has a low surface tension. Spraying it is simple, and it dries rapidly.

By esterifying cellulose with acetic, butyric, and anhydrides, cellulose is converted to cellulose acetate butyrate (CAB). When cellulose is entirely soluble in the solvent, CAB synthesis is carried out under homogenous conditions. A significant commercial cellulose derivative product called cellulose acetate butyrate (CAB) has been employed in coating materials, optical films, filtration membranes, and polymers (Dehmen, 2018). The most versatile cellulose ester type, CAB Solvent has an optimum solubility and is compatible with other popular paint polymers. Esters, ketones, glycol ethers, glycol ether esters, aromatic hydrocarbon solvents, and combinations of alcohols are among the solvents in which it is soluble (Turkchem, 2017). Its water-soluble versions are utilized to produce leather. The surfaces made from CAB aid in the manufacturing of relatively high levels of flexible, abrasion-resistant, high-gloss, and flame-resistant leather by both leather and artificial leather manufacturers (Cellulosic Resins and Their Uses, 1972).

In this investigation, white finishing-process dye was applied to chrome-tanned bovine crust leathers, and color measurements were taken. Then, three different topcoats - Polyurathane (PU), Nitrocellulose (NC), and Cellulose Aceto Butyrate—were applied, and the color was once more measured. It was determined whether there had been a color change between before and after the topcoat using the findings of the color measurement. As a result, the impact of the topcoat on color change was examined.

https://doi.org/10.24264/icams-2022.III.7

EXPERIMENTS

Finishing Applications

Bovine crust leathers that had been chrome-tanned were employed in this study. The leathers used for the study were finished using the recipe listed in Table 1.

Table 1. Finishing recipe

	Formula		Notes
Product	1	2	
VDB-2 1004	150		Verpol White Pigment
AA 4750	50		Piel Color Synthetic Waks
UR 1443	100		Piel Color Aliphatic Polyurethane
RE 2350	70		Piel Color Acrylic Polymer
Water	200	100	
UR 1786*		100	Piel Color Polyurethane Top Coat
LA 6016**		100	Piel Color NC Hydrolac
LW 5343***		100	Stahl CAB Hydrolac

Application :
1) 3xspray - hydraulic press 90C/90 bar- 4xspray
2) 2xspray -hydraulic press 100C/100 bar
*Experiment 1
**Experiment 2
***Experiment 3

Referring to the lacquer coat's color measurements all leathers were finished with the same white base coat and the color was measured.The Experiment 1 leathers received a water-soluble Polyurethane topcoat (UR 1786), the Experiment 2 leathers received Nitrocellulose hydrolac (LA 6016), and the Experiment 3 leathers received Cellulose Aceto Butyrate Hydrolac (LW 5343). All leathers were then measured for color once again to to compare the color change.

Color Measurement Tests of Leather Samples

Color measurement was carried out twice, after the paint coat (first measurement) and after the topcoat was applied (Experiment 1, Experiment 2 and Experiment 3). Color difference determination was realized on Konica Minolta brand CM 3600d Spectrophotometer. Firstly, Standard white calibration process was practised in device. Measurement was carried out by reading 15 points from the grain surface of the samples into the reading area of the instrument. The results were reported as average values of these measurements.

Statistical Evaluation of Results

While evaluating the findings obtained in the study, NCSS (Number Cruncher Statistical System) 2022 Statistical Software (NCSS LLC, Kaysville, Utah, USA) program was used for statistical analysis. Dunn's test was used to determine the group that caused the difference.

https://doi.org/10.24264/icams-2022.III.7

RESULTS AND DISCUSSION

In color measurements, evaluations were made according to the ΔE*ab (D65) results obtained from L* a * b color area measurements. Various quantitative methods have been developed to avoid the complexity that arises in the verbal expression of the concept of color. L* a * b color space, defined by CIE (International Commission on Illumination) in 1976, is widely used in color measurements. In this method, the L aperture indicates the +a red direction, -a the green direction, +b the yellow direction and -b the blue direction. ΔE*ab is the numerical value showing the size of the color difference (Turkchem, 2017)

In this study, ΔL values were compared to measure the lightness change of leather samples and ΔE values were compared to measure the total color change.

Comparison of ΔL Measurement Results

Comparison of ΔL results of leather samples is given in Table 2.

Table 2. Comparison of ΔL Values (Kruskal-Wallis Multiple-Comparison Z-Value Test (Dunn's Test))

Section 1			
Variable	ΔL Experiment 1	ΔL Experiment 2	ΔL Experiment 3
ΔL Experiment 1	0.0000	3,3723	0,9882
ΔL Experiment 2	3,3723	0.0000	2,3841
ΔL Experiment 3	0,9882	2,3841	0.0000
First_measurement	4,0258	0,6535	3,0377

Section 2	
Variable	First_measurement
ΔL Experiment 1	4,0258
ΔL Experiment 2	0,6535
ΔL Experiment 3	3,0377
First_measurement	0.0000

Regular Test: Medians significantly different if z-value > 1,9600.
Bonferroni Test: Medians significantly different if z-value > 2,6383.

According to the Table 2, a significant difference was found in the Experiment 1 and Experiment 3 compared to the first measurement. Based on this information, it can be said that Polyurethane and Cellulose Aceto Butyrate topcoat materials change the degree of lightness.

Comparison of ΔE Measurement Results

The ΔE results of the leather samples are given in Table 3.

https://doi.org/10.24264/icams-2022.III.7

Table 3. Comparison of ΔE Values (Kruskal-Wallis Multiple-Comparison Z-Value Test (Dunn's Test))

Section 1 Variable	First_measurement	ΔE Experiment 2	ΔE Experiment 3
First_measurement	0.0000	0,1621	4,104
ΔE Experiment 1	0,1621	0.0000	3,9419
ΔE Experiment 2	4,104	3,9419	0.0000
ΔE Experiment 3	0,481	0,3189	3,623

Section 2 Variable	ΔE Experiment 3
First_measurement	0,481
ΔE Experiment 1	0,3189
ΔE Experiment 2	3,623
ΔE Experiment 3	0.0000

Regular Test: Medians significantly different if z-value > 1,9600.
Bonferroni Test: Medians significantly different if z-value > 2,6383.

According to the Table 3, a significant difference was found between the first measurement and the second Experiment 2. According to this information, it can be said that Nitrocellulose topcoat material change the color.

CONCLUSION

Finishing practitioners have noticed that some topcoat materials change color during the finishing process, which is the final stage of leather production in which various performance properties and the final color are applied to the leather. In order to investigate this situation, to reformulate with the finishing process in this study, and color measurement analyses were performed. Three different topcoats were applied to leather samples, namely Polyurethane, Nitrocellulose, and Cellulose Aceto Butyrate, and color measurements were taken again. Statistical methods were used to compare all color measurements taken. According to the statistical evaluation results, the topcoat materials Polyurethane and Cellulose Aceto Butyrate changed the whiteness of the leathers measured as lightness difference. The Nitrocellulose topcoat material was found to change the color of the leathers.

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https://doi.org/10.24264/icams-2022.III.7