Application of L-Ascorbic Acid as an Antioxidative Colorment in Leather Finishing

by

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Abstract

In this study, chrome tanned bovine crust leathers were dyed white during finishing process. Experiments with 1%, 2%, 3%, 4% and 5% L-ascorbic acid addition were performed on the finishing layer of the finishing application. L-ascorbic acid was not added to the control group and processed according to the standard method. After these processes, color measurement analyzes were performed on Konica Minolta CM 3600d spectrophotometer. In order to investigate the effects of L-ascorbic acid on other performance properties of leather, light fastness test according to TS 1008 EN ISO 105-B02 (2001 TS EN ISO 11640 2001) and dry rub fastness test according to standard method were performed. The results of the study were statistically evaluated according to the NCSS (Number Cruncher Statistical System) method. As a result of the research, it was observed that L-ascorbic acid gave a pearly pink color to the leathers. It was found that the dry rubbing fastness of the leathers treated with L-ascorbic acid improved. In the light fastness tests, the results of the experimental group leathers were recorded better by the blue scale.

Introduction

Leather production, which is a by-product of the meat industry, is a traditional industry that has existed since ancient times and using animal skin is one of the oldest technologies of humanity.[1] According to the final product (clothes, shoes, upholstery, saddlery etc.) chemical (soaking, unhairing-liming, deliming, bating, degreasing, pickle, tanning, basification, neutralization, dyeing, lubrication, retanning, finishing) and mechanical (fleshing, shaving, drying, ironing-press) covers a number of processes.[2,3] The desired surface properties (color, glossy or matt appearance, slippery, etc.) to the leather by the finishing process and the performance characteristics that provide protection against external factors (light fastness, rubbing fastness, resistance to solvents etc.) and become available for sale.[4] For this purpose pigments, aniline dyes, binders (acrylic, polyurethane, butadiene etc.), waxes, touching agents, lacquers (polyurethane, nitrocellulose), various organic solvents and cross-linkers (polyaziridines, isocyanates and polycarbodiimides) are used.[5,6]

L-ascorbic acid is a powerful water-soluble antioxidant.[7] It protects some oxidizable compounds with its reducing effects as free radicals and oxygen annihilator. L-ascorbic acid is used in skin care products in the cosmetic industry and as an additive in the food industry.[8,9]

Koochakzaei et al. in their research on the stability of silicone oil and polyethylene glycol; they used L-ascorbic acid to increase the effectiveness of polyethyleneglycol.[10] According to Devikawati et al. used ascorbic acid, gallic acid, tara, mirobalan and keratin-based protein hydrolyzate to prevent the carcinogenic effects of hexavalent chromium. The results of the research show that the use of Ascorbic acid during descaling, pickling and tanning is more effective in preventing the formation of hexavalent chromium.[11] Kothandam et al. synthesized nano-sized copper and used ascorbic acid as an oxidation inhibitor during copper synthesis in their study investigating the effects of this substance on leather performance properties in the finishing of shoe upper leathers. In addition, researchers state that ascorbic acid is generally used in nanotechnology applications during copper synthesis and storage.[12]

As can be seen from the above mentioned studies in the leather industry, L-ascorbic acid is not widely used. Leather production effect on the leather and chemicals used in the interaction is a subject that is open to research. Since it is a known fact that dyes, like most chemicals used in leather production, may have some harmful effects, alternative materials are needed. Therefore, in this study, it was aimed to benefit from coloring ability of L-ascorbic acid, which is known for its antioxidant properties.

Experiments

Finishing Applications

In this research, chrome tanned undyed bovine crust leathers were used. L-Ascorbic acid powder form used in experiments. Finishing recipe is shown Table I.

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Table I
Finishing recipe used in application

Chemicals	Application 1. Coat (grams)	Application 2. Coat (grams)	Explantion
Akral PU Soft	220		Mixture of acrylic and polyurethane binders (Alpa Kimya)
Ground Plus A	50		Synthetic wax (Alpa Kimya)
Akrederm 1193	100		Acrylic Binder (Alpa Kimya)
SFT-MV-1	85		Wax-polyamide mixture(Alpa Kimya)
RPU 2260	50		Polyurethane Binder(Stahl Kimya)
PP 25838	100		White pigment(Stahl Kimya)
HM 443	7	10	Silicone touch (Stahl Kimya)
Water	290	100	
LW 21016		100	Hydrolacs (Stahl Kimya)
L-Ascorbic Asid		X	

1) 6xspray- Roto Press(80°C, 150 Bar)-4xspray- Roto Press (80°C,70 Bar)-3xspray
2) 2xspray- Roto Press(90°C- 70 Bar)

After the first coat application of the finishing recipe, each leather divided into three parts. The amount indicated by X in the second coat solution, the total solution and 0%, 1%, 2%, 3%, 4% and 5% of the leathers were added. Each experiment has three replicates was carried out. All leathers are conditioned for reproducible tests in the laboratory under equal conditions (20 ± 2°C 65 ± 2% RH).

Dry Rubbing Fastness Analyses

Leather samples were tested with black colored felt and dry rub fastness tests according to TS EN ISO 11640 (2001) from the grain surface. Otto Specht Bally Finish Tester device used for analysis. Color changes in leather samples and felts were evaluated according to ISO 105-A02 (1996) and ISO 105-A03 (1996) standards and ISO 105 standard with Gray scale.

Color Measurement Tests of Leather Samples

Color fastness determination was realized on Konica Minolta brand CM 3600d Spectrophotometer. Firstly, Standard black and white calibration process was practiced in device. Measurement was carried out by reading 5 points (4 corner points and 1 mid-point) from the grain surface of the samples into the reading area of the instrument. The results were evaluated by averaging these 5 measurement sites.

Light Fastness Analysis

Light fastness determinations were analyzed according to TS 1008 EN ISO 105-B02 (2001) standard for 24 hours by ATLAS brand ALPHA model xenon arc light fastness test device. The results were evaluated with blue scale.

Statistical Evaluation of Results

While evaluating the findings of the study, statistical analysis NCSS (Number Cruncher Statistical System) 2007 Statistical Software (NCSS LLC, Kaysville, Utah, USA) was used. While evaluating the study data, Kolmogorov Smirnov test and boxplot graphs were used to evaluate the suitability of the quantitative data for normal distribution as well as descriptive statistical methods (average, standard deviation, median, frequency and ratio). Normal distribution of parameters between groups One-way Anova test and Bonferroni test for detecting the difference group; Student's t-test was used in their evaluations according to two groups. Between groups of non-normal distribution of parameters Wallis test and Dunn test in detecting the difference group; Mann Whitney U test was used in evaluations according to two groups. In comparison of qualitative data, Fisher Freeman Halton test was used. The results were evaluated at 95% confidence interval and $p < 0.05$ significance level.

Results and discussion

Results of the appearance of leather

The leathers were subjected to visual evaluation after the application. After the use of L-ascorbic acid, different tones from yellow to pink were observed in the leathers. Figure 1 shows these color differences.

Dry rubbing fastness results

In accordance with the standard method, dry rubbing fastness analysis of the leathers were made using black colored felts. The

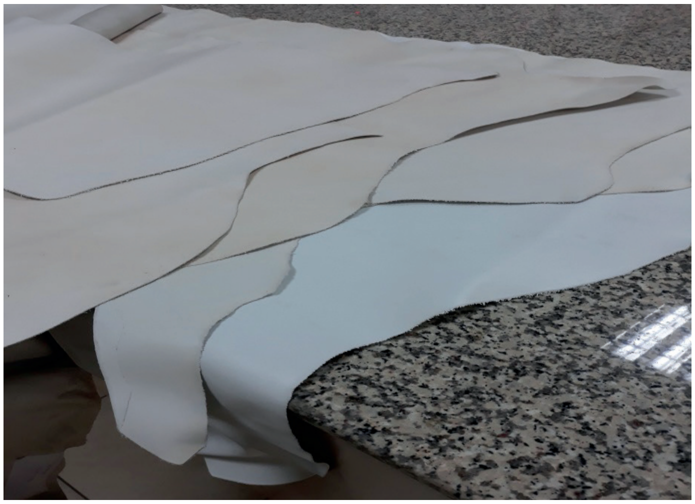

Figure 1. Color change observed in leather samples after finishing

results were evaluated on a gray scale. According to the results of both felt and leather color changes occurred between 1 and 5 points were given. A value of 5 indicates no spotting and a value of 1 indicates extreme spotting.

The results of dry rub fastness evaluation showed a statistically significant difference between leather and felt between control and experimental groups ($p < 0.01$). Dry rubbing fastness results were higher in the experimental group.

Color measurement analysis results

The color measurements will be evaluated according to DE * ab (D65) results obtained from L * a * b color areas measurements. Table III shows that color measurements evaluation results.

In our study, a statistically significant difference was found between the color measurements of the control and experimental groups ($p < 0.01$); D65 levels were significantly higher in the experimental group. D65, which is also a color criterion, showed statistically significant difference in the evaluation results according to L-ascorbic acid ratios in the experimental group ($p < 0.001$). There was no significant difference between 1% L-ascorbic acid and 2% L-ascorbic acid color measurements ($p > 0.05$); The D65 color value obtained in those using 1% L-ascorbic acid was significantly lower than those using 3% and 4% (p: 0.001; p: 0.001); There was no significant difference between 5% and 1% in color ($p > 0.05$).

Table II

Evaluation of dry rub fastness test results

		Control	Experimental		
		n(%)	n(%)	Test Value	p
Leather	3	3 (100)	0 (0)		
	4/5	0 (0)	3 (20)		
	5	0 (0)	12 (80)	11.889	0.002**
Felt	3/4	3 (100)	0 (0)		
	4	0 (0)	3 (20)		
	4/5	0 (0)	12 (80)	11.889	0.002**

Fisher Freeman Halton test **p<0.01

Table III

Color measurement evaluation results

	Control		Experimental	
	Median (min-max)	Ort+SD	Median (min-max)	Ort+SD
L*(D65)	93.3(90.9/94)	93.19±0.74	90(86.2/91.5)	89.6±1.24
a*(D65)	-1.1(-1.3/-1)	-1.09±0.06	1.1(-0.1/2.6)	1.18±0.75
b*(D65)	2.5(1.7/3.2)	2.44±0.3	9.3(6.1/15.4)	9.69±2.34
dL*(D65)	-4.9(-8/-2.9)	-4.66±1.25	-8.3(-12.6/-5.4)	-8.25±1.6
da*(D65)	-1(-1.2/-0.9)	-0.98±0.07	1.2(0/2.7)	1.29±0.75
db*(D65)	2.8(2/3.4)	2.74±0.3	9.6(6.5/15.7)	9.99±2.34
dE*ab(D65)	5.7(4.1-8.5)	5.54±1.05	12.3(8.8-20.2)	13.08±2.67

Table IV

Evaluation results of color measurements according to L-ascorbic acid ratio

		n	dE*ab(D65) Median (min-max)	Ort+SD	Test Value	p
	Control	30	5.7(4.1/8.5)	5.54±1.05		
Group	Experiment	150	12.3(8.8/20.2)	13.08±2.67	15.165	[a]0.001**
					58.55	[b]0.001**
						Post Hoc;
						%1-%3 p:0.001
						%1-%4 p:0.001
	1% L-Askorbic Asid	30	12.1(9.2-15.8)	12.16±1.53		%2-%3 p:0.001
	2% L-Askorbic Asid	30	11.3(8.8-14.6)	11.41±1.42		%2-%4 p:0.001
	3% L-Askorbic Asid	30	17.2(10.7-20.2)	16.75±2.39		%3-%4 p:0.001
	4% L-Askorbic Asid	30	14(9.8-17.1)	13.98±1.61		%3-%5 p:0.001
L-Askorbic Asid	5% L-Askorbic Asid	30	10.9(9-13.4)	11.08±1.18		%4-%5 p:0.001

[a]Student t test [b]Oneway Anova test & posthoc Bonferroni test **p<0.01

D65 color measurements were significantly lower in 2% L-ascorbic acid use compared to 3% and 4% (p: 0.001; p: 0.001); No significant difference was found between 2% and 5% (p> 0.05). The use of 3% found the highest D65 color measurement and was significantly higher than 4% and 5% (p = 0.001; p: 0.001). Color measurements obtained by using 4% L-ascorbic acid were found to be significantly higher than 5% usage.(P = 0.001).

Light fastness test results

Table V shows the results of light fastness analyzes. Evaluation of blue scale used in light fastness test results showed statistically significant difference between control and experimental groups (p <0.01). The results of experiments evaluation were found to be better than the control in the blue scale.

Conclusion

In this study, the applicability of L-ascorbic acid, an antioxident, as an alternative to colorments used in the leather industry was investigated. For this reason, chrome-tanned undyed crust leathers are dyed white in the finishing process. In the finishing layer, L-ascorbic acid material was added to the finishing solution at the rates of 1%, 2%, 3%, 4% and 5% L-ascorbic acid. These processes were repeated 3 times and compared with leathers treated according to the standard method without L-ascorbic acid. In these comparisons, visual evaluation, color measurement, rubbing fastness and light fastness were analyzed according to standard methods. Analysis results show that L-ascorbic acid gives the leather a pearly pink color tone while improving dry rubbing fastness and light fastness properties. For this reason, it has emerged that it can be used as a new colorment in leather finishing.

Table V

Light fastness assessment results

		Control n(%)	Experiment n(%)	Test Value	p
Blue scale	1	3 (100)	0 (0)	11.717	0.001**
	1/2	0 (0)	1 (6.7)		
	2	0 (0)	7 (46.7)		
	3	0 (0)	7 (46.7)		

Fisher Freeman Halton test **p<0.01

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