ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

COLOR AND PHYSICAL PROPERTIES OF LEATHER VIA EXTREME OZONE BLEACHING APPLICATIONS

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Abstract: *Bleaching is a good way for the preparation of fiber based products to remove the colored impurities. However, conventional bleaching processes pollute the water with chemical components and suspended solid particles. Ecological concerns have prompted to search for new solutions to reduce the environmental pollution. This work aims to cleaner bleach the skin surface problems and color with ozonation process and to examine the possible physical and chemical effects on leather products under heavy process applications. In this perpective, decolorization procedure was carried out on the leathers having dyeing spots by different bleaching time of the ozonation process. The effect of ozonation time (45, 60 and 90 min) and water pick-up value (WPV) (0% and 50%) were investigated for decolorization effect on dyed leather products. After decolorizing procedure, color difference and K/S (color strength) values on leathers was spectrophotometrically measured by Konica Minolta CM-3600d testing apparatus. Extreme ozone bleaching under long proess duration was examined in terms of the strength properties of leather. Structural changes were also determined via Cr(VI) analysis after ozonation process. 90 min ozonation application provided the best bleach with 0% WPV and 50% WPV, on the other hand, 90 min as the heaviest ozone bleach condition negatively affected the physical properties of leather.*

Key words: Leather, ozone, bleaching, physical properties.

1. INTRODUCTION

Tanning and dyeing processes in leather production steps; they are processes that are sensitively emphasized in terms of economic, ecological and engineering applications. Tanning agents penetrate into the collagen fibers of the skin, form bonds with the active groups of amino acids, and increase the hydrothermal stability of the proteinic structure. In order for the tanning process to be carried out effectively, the tanning agent must be able to penetrate the three-dimensional fiber structure of the leather at the highest rate and react with collagen. Tanning processes that are not carried out under suitable conditions result in serious surface defects. Considering that approximately 90% of the leathers produced in the world today are tanned with chrome, chromium surface stains which are frequently encountered are an important issue that should be emphasized and resolved. [1-3].

Stained surface appearance in leather products can be also occured because of the defects in dyeing process. Fast fixation, insoluble dyestuffs, inaccurate temperature of the dyeing float and pH adjustment for neutralization can cause the undesirable impurities on leather surface. Thus, homogeneity in color is destroyed. Therefore, bleaching is required for the preparation of fiber based products to remove the colored impurities [4,5].

Various stains that occur in leather production cause companies to have problems in fixing the color on the finished leather and as a result, cause significant economic losses. In the industry, an intensive application is made in the finishing process for such leathers, and discolorations are tried to be covered. However, at the end of this intense finishing application, the leather loses its natural appearance and at the same time its attitude. This causes a decrease in the economic value of leathers. At the same time, these finishing processes applied to cover color errors are reflected as an extra cost to the companies and are not seen as a practical solution [6].

Bleaching is a good way for the preparation of fiber based products to remove the colored impurities. Besides the production of fiber-based products, the bleaching process has great importance to achieve white leather products. However, conventional bleaching processes pollute the water with chemical components and suspended solid particles. Ecological concerns have prompted to search for new solutions to reduce the environmental pollution. For this purpose, much effort has been made to achieve more environmentally friendly production processes [7,8].

Ozone application was successfully implemented in various attempts for leather processes in recent years [8,9]. This work aimed to bleach the skin surface problems and color with heavy ozonation process and to examine the possible physical and chemical effects on leather products.

2. EXPERIMENTAL PART

2.1. Materials

As a leather material, chrome tanned and black dyed domestic sheepskins were used before the finishing process. All used chemicals in this study were of laboratory commercial grade.

2.2. Ozonation process

The equipment used for ozonation has three components; the ozone generator, the applicator, and the ozone destroyer. The system is fully closed because of the harmful effects of ozone on health. The laboratory-scale ozonator (Lundell Aquametrics, Inc.) with 180 mg/h capacity was used in experiments. Oxygen is supplied to the generator from an oxygen tube and the flow rate of ozone was set at 3 L/min. The applicator is a cylindrical glass tube with a diffuser at the bottom. The dimension of the applicator is 12 cm in diameter and 15 cm in height.

The effect of the treatment time during ozonation was researched. Treatment times were set at 45, 60 and 90 min, respectively. During these experiments, firstly, the leather samples were in dry form without any additional soaking process to increase the moisture content (0% WPV). Second, the effect of moisture content in leathers described as WPV% on the decolorization efficiency was investigated. To this end, the samples were soaked in water at pH7; after that, the WPV of the samples was set at 50% with squeezing rollers and drying oven.

2.3. Colorimetric measurements

The color coordinates of control and operated samples with ozonation were measured on a Konica Minolta CM-3600d Spectrophotometer from 360-700 nm under a D65/10^o illuminant (D65 illuminant, specular included, 10^o observer angle). The percent reflectance values (at λ_{max}=400 nm) were recorded and color strength values (*K/S*) were calculated according to Kubelka-Munk formula (Eq. (1)), which is shown below.

$$K/S = (1-R)^2 / 2R \qquad (1)$$

where *K* is the scattering coefficient, *S* is the absorption coefficient, *R* is the reflectance.
where, *R* is the decimal fraction of the reflectance of dyed fiber.
where *R*=1.0 at 100% reflectance.

Spectrophotometric data for control and operated leather samples were used for color difference calculations. Color difference values were obtained according to the CIELAB (1976) equation [10] as follow (Eq. (2)):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (2)$$

The colors are given in CIEL**a*b*;*

Coordinates: *L**corresponding to the brightness (100 = white, 0 = black), *a** to the red-green coordinate (+ = red, - = green) and *b** to the yellow-blue coordinate (+ = yellow, - = blue).

2.4. Strength analyses of final products

Prior to the analyses all finished leathers were conditioned according to the standard of EN ISO 2419 [11] and sampling was done in accordance with the standard of EN ISO 2418 [12]. The final products were subjected to the tests of tensile and tear strength. Shimadzu AG-IS testing device was used for all analyses. Thickness measurement of the samples was performed in accordance with EN ISO 2589 [13], tensile strength with EN ISO 3376 [14] and tear load with EN ISO 3377-2 [15].

2.5. Chromium(VI) analysis

Chromium(VI) analysis in leather samples was performed in triplicate according to IUC 18 (EN ISO 17075 2007) [16] standard before and after ozonation applications. This analytical method is based on the reaction of chromium(VI) with diphenylcarbazide and subsequent colorimetric determination at 540 nm by using a double-beam Shimadzu 1601 UV-Visible region spectrophotometer.

2.6. Statistical analyses

The results were evaluated statistically by using One-Way ANOVA, descriptive statistical and Duncan tests at SPSS 15.0 statistical software package. All data were represented as mean for three independent measurements. Comparison of means was analyzed by Duncan test and differences were considered as significant when $p<0.05$.

3. RESULTS AND DISCUSSION

Utilizing ozone for bleaching processes is used a means of decreasing the environmental impact. Ozone (O_3) has an oxidation potential of 2.07 eV, which is higher than that of the widely used bleaching agent, hydrogen peroxide (1.77 eV). Ozone is available as molecular ozone at acidic pH. It decomposes into secondary oxidants in alkaline pH. Ozone has been successfully used for color removal from textile and leather industry effluents [17,18]. Ozone has also been successfully applied for cotton, jute, linen, wool, angora, denim, soybean, nettle fiber bleaching in recent years [19-24]. However, there is an only literature for decolorization of leather products by ozone application [8].

Ozone can effectively decolorize the dye by breaking the conjugated double (–N = N–) bonds. Ozone cleaves the unsaturated bonds in aromatic molecules found in humic substances, the chromophores of the dyes and other pigmented compounds, thereby reducing the color. The mechanism of the reaction of ozone follows two main pathways, a direct path corresponding to the action of molecular ozone and an indirect path corresponding to the action of free radicals species resulting from the decomposition of ozone in water [18].

Onem et al. (2017) [8] indicated the effectiveness of ozonation process on leathers. 30 min ozonation application provided the best whiteness on the leathers. There was no any structural deformation and strength lose for the ozonated leathers after 30 min duration. This study aimed to examine extreme ozonation conditions for decolorizing effect and physical properties of leather. Table 1 shows the color values of the leather samples before and after ozonation process for 0% WPV application.

Table 1: *Color values of the leather samples before and after ozonation process for 0% WPV*

Ozonation time	**Color values**			
	L	*a**	*b**	*ΔE*
Control sample	24.11±0.39	1.76±0.3	3.31±0.21	-
45 min	32.50±0.41	0.02±0.17	3.71±0.28	8.58
60 min	37.12±0.12	0.67±0.08	6.21±0.19	13.37
90 min	41.16±0.21	1.92±0.18	3.51±0.19	17.05

Table 1 provides the increased *ΔE* values with increased ozonation duration. 17.05 of *ΔE* value was obtained compared to the control leather sample. Higher *L* values also indicate the more whiteness of leathers. Table 2 shows the color values of leather samples before and after ozonation process for 50% WPV application.

Table 2: *Color values of the leather samples before and after ozonation process for 50% WPV*

Ozonation time	**Color values**			
	L	*a**	*b**	*ΔE*
Control sample	24.11±0.39	1.76±0.3	3.31±0.21	-
45 min	36.11±0.36	1.55±0.17	8.21±0.25	12.96
60 min	42.00±0.42	2.0±0.21	11.71±0.21	19.77
90 min	49.81±0.51	4.63±0.37	16.31±0.39	28.94

Table 2 also proved the higher *ΔE* values when ozonation duration was long. 90 min ozonation application gave the highest *L* value and *ΔE* value. Moreover, 90 min ozonation process with 50% WPV gave the better results than 0%WPV according to the whiteness degree of leathers. *L* value came from 24.11 before ozonation to the 49.81 after bleaching process. *ΔE* was 28.94 with 90 min application under 50%WPV.

Fig. 1 demonstrates the color strength (*K/S*) values of ozonated leather samples with 0% and 50% WPVs. Low *K/S* value defines more whiteness properties of leathers. That means better bleashing process by ozonation.

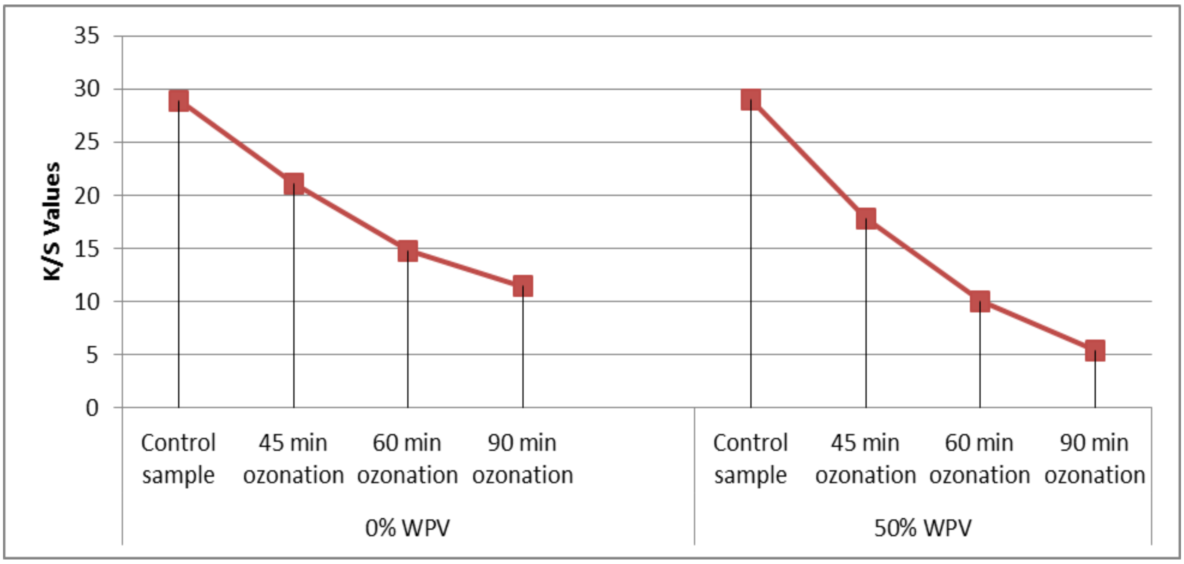

Fig. 1. *Color strength (K/S) values of ozonated leather samples with 0% and 50% WPVs*

90 min ozonation application under 50% WPV showed the closest whiteness value in Fig. 1 as well. Color strength of leather before ozonation was 28.97 with *K/S* indicator. The closest whiteness after bleaching was obtained as 5.42 via the heaviest ozonation application.

Table 3 and Table 4 show the physical strength properties of leathers before and after ozonation under 0% and 50% WPVs.

Table 3: *Strength test results of the untreated and ozonated leather samples under 0% WPV*

Process	**Tensile strength**	**Tear strength**
Before bleach	10.16 ± 2.12^{a}	35.02 ± 3.23^{a}
45 min ozonation	9.95 ± 2.13^{a}	32.91 ± 3.16^{a}
60 min ozonation	9.57 ± 0.88^{a}	32.14 ± 4.09^{a}
90 min ozonation	9.12 ± 1.91^{b}	30.11 ± 1.77^{b}

a, b; values in the same column with different superscript letters are significantly different (p<0.05).

Table 4: *Strength test results of the untreated and ozonated leather samples under 50% WPV*

Process	**Tensile strength**	**Tear strength**
Before bleach	10.16 ± 2.12^{a}	35.02 ± 3.23^{a}
45 min ozonation	9.89 ± 2.12^{a}	32.90 ± 3.16^{a}
60 min ozonation	9.61 ± 0.99^{a}	31.99 ± 4.07^{a}
90 min ozonation	9.01 ± 1.79^{b}	30.12 ± 3.87^{b}

a, b; values in the same column with different superscript letters are significantly different (p<0.05).

Table 3 and Table 4 proved the decreased strength values with the increased ozonation time. 0% WPV and 50% WPV gave the similar results and correlations. Only 90 min ozonation duration negatively affected the strength properties of leathers statistically. Decreases after 90 min bleaching process were important levels when $p<0.05$ for both dry samples and wet samples. Each ozonation type and duration decreased the physical properties, but they were negligible except of the longest time as the heaviest process.

Essentially 90% of leather products are tanned by chromium salts in the worldwide because of the indispensable features of the given properties of chromium salts for leather products. Conventional bleaching was not applied to leather in this study because conventional oxidative bleaching agents have a big potential to convert Cr(III) in leather to Cr(VI) by oxidation [25-27]. The formation of such materials in leather may cause leather products, such as garment, upholstery and shoe lining, having direct contact with the human body to affect human health seriously. Cr(VI) formation in leathers was also analyzed in our study before and after ozonation applications in case any oxidation formation. The results showed that Cr(VI) contents of the leathers were under 3 ppm. Leathers with this value are in safe because international regulations reported that Cr(VI) content should be under 3 ppm to avoid the ecological risks for the leather goods [25-27]. This result also proved the safe bleaching process and safe product as the environmentally friendly decolorization method.

Moreover, conventional bleaching processes pollute the water with chemical components and suspended solid particles. Ecological concerns have prompted to search new solutions to reduce the environmental pollution in leather industry and sustainable ways are being discovered especially in the recent years. That’s why environmentally friendly and safe decolorization processes for leather products are needed. Ozonation of leather products is a great opportunity to remove the chromium and dyeing defects from the surface. In that aspect, the ozonation method is more novel for the leather indutry compared to textile industry, because conventional methods are highly risky on leather products.

Acknowledgements

This study is supported by Ege University Scientific Research Projects Coordination Unit. The authors would like to thank Ege University for the financial support provided (Project No: FLP-2021-23239).

4. CONCLUSIONS

Defected leathers having impurities on the surface are poor in terms of the aesthetics and resulted with low prices in sales for the companies. This situation pushes the companies to find the new and innovative solutions. Therefore, such surface defects should be prevented before finishing with the effective ways. These effective ways should also be environmentally friendly in terms of the strict stipulations by the leather industry players and important organizations. Green solutions are being more important day by day. European Green Deal should be taken into consideration for many industrial applications.

Ozonation to decolorize leather products was investigated as a novel bleaching method via this research under respectively heavier conditions compared to the previous literatures carried out for leather products. Leather products were successfully decolorized by ozonation with different durations under increased process time and water pick-up conditions. The water pick-up value of leather samples was found as important parameter in terms of the achieved decolorization effect. The occurred strength loss after prolonged ozonation times was negligible except of the 90 min applications. There was also no problem for the Cr(VI) formation by ozone bleaching process. This study showed the usability, benefits and small disadvantages of ozonation to decolorize the leather products. Studies on an industrial scale should be performed related to the application of ozonation for the leather sector in terms of the cleaner processing ways.

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