

DETERMINATION OF SOME PHYSICAL CHARACTERISTICS OF ARTIFICIALLY AGED CHROME TANNED GARMENT LEATHER

SUNİ OLARAK YAŞLANDIRILAN KROMLA TABAKLANMIŞ GİYSİLİK MAMUL DERİLERİN BAZI FİZİKSEL ÖZELLİKLERİNİN BELİRLENMESİ

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ABSTRACT

The aim of this study was to determine the physical changes that might occur in chrome-tanned garment leathers with artificial ageing. For this purpose, a study was conducted on eight pieces chrome-tanned sheep leathers for garment. All leathers were artificially aged by employing the ageing factors of temperature, temperature + UV ray and temperature + humidity. Then, the changes that occurred in the characteristics of artificially-aged leathers were determined by means of some physical tests. According to the findings, it was ascertained that the artificial ageing factors of temperature + UV ray, temperature, and temperature + humidity (in a descending order) caused significant losses of quality on garment leathers. Moreover, decrease in the tensile strength and tear load, fall in the shrinkage temperature and fading in the color of the artificially-aged garment leathers were ascertained.

Key Words: Garment leather, Artificial ageing, Ageing factors, Physical change, Leather industry.

ÖZET

Bu araştırmada; suni yaşlandırma ile krom tabaklanmış mamul giysilik derilerde meydana gelebilecek olan fiziksel değişimlerin belirlenmesi hedeflenmiştir. Bu amaçla, sekiz adet kromlu mamul giysilik koyun derisi üzerinde çalışılmıştır. Bütün derilere sıcaklık, sıcaklık+UV ışığı ve sıcaklık+nem yaşlandırma faktörleri kullanılarak suni yaşlandırma işlemi yapılmıştır. Daha sonra, suni yaşlandırma yapılan derilerin özelliklerinde meydana gelen değişimler bazı fiziksel testler ile belirlenmiştir. Elde edilen bulgulara göre; büyükten küçüğe doğru sıcaklık+UV ışığı, sıcaklık ve sıcaklık+nem suni yaşlandırma faktörlerinin giysilik deriler üzerinde kayda değer kalite kayıplarına sebep olduğu belirlenmiştir. Suni yaşlandırma işlemine tabi tutulmuş giysilik derilerin çekme mukavemeti, çekme uzaması ve yırtılma yükünde azalma, renginde solma, büzülme sıcaklığında ise düşme tespit edilmiştir.

Anahtar Kelimeler: Giysilik deri, Suni yaşlandırma, Yaşlandırma faktörleri, Fiziksel değişim, Deri sanayi.

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1. INTRODUCTION

Performances expected from leathers that are made into an indefectible product through tanning process and from leather products that are produced from these leathers decrease in the process of time as a result of not only the effect of environmental conditions such as heat, light and humidity but also chemical actions and mechanical strains. Ageing is defined as the change that occurs in the course of time in the

performance values of goods and the loss of some of their characteristics (1, 2). It is technically important to observe the development of ageing process and to predict probable loss of characteristics and also to determine degradation products. Ageing time depends upon material's structural characteristics and environmental factors.

Upon the change of atmospheric conditions such as UV rays, temperature and relative humidity,

which are among the most significant environmental factors that affect materials' structural characteristics, leather material's physical and chemical characteristics may change and performance may decrease (3,4). Due to its fibrous network tissue, leather's strength characteristics are affected by changing atmospheric conditions more than all other goods.

As the signs of ageing, in the course of time, leathers' surface characteristics change and strength characteristics

worsen, malodors occur in consequence of fat decomposition, losses emerge in hydrothermal stability with the decomposition of tanning, changes occur in the appearance of leather, and quality losses such as color fading/yellowing are encountered (5-9).

In the leathers, reversible and irreversible ageing changes may end up with both chemical and physical results. Odor and appearance changes and mechanical characteristic changes are called physical ageing while polymer structure and characteristic changes and tanning agent structure and characteristic changes are called chemical ageing (2, 10).

The aim of this study was to artificially age chrome-tanned garment leathers by applying temperature, humidity and UV ray, which are significant ageing factors, to determine the physical changes in these leathers as a consequence of the physical ageing that occurred, and to reveal the external factors that affected the physical characteristics of garment leathers and how and to what extent they affected.

2. MATERIAL AND METHODS

2.1. Material

In this study, eight pieces of finished garment leathers tanned by chrome were used as material. These materials were obtained from Çetinkaya Fur Leather and Garment Ltd. operating in The Organized Leather Industrial District in Istanbul, Turkey.

2.2. Methods

Before the garment leathers used in the research were artificially aged, due to the fact that leather is an expensive material and that the two half pieces of leather which are obtained as one piece of leather is cut in parallel with

the backbone have bilateral symmetry, they were cut into two equal pieces in parallel with the back line and thus made into sides (11). After one of the sides was set apart as control group, five sides were randomly selected for each ageing factor and thus three groups were created and each side was separately numbered.

Artificial Aging Process of Garment Leathers

Research materials were artificially aged by applying temperature, temperature + humidity and temperature + UV radiation aging factors according to TS EN ISO 17228 (2009) (12). Experimental design was shown in Table 1.

Physical Tests of Garment Leathers

In order to evaluate the physical changes of chrome tanned garment leathers, shrinkage temperature (13), tensile strength and percentage extantion (14) and tear load (15) tests were examined.

Color Evaluation Test of Garment Leathers

Konica Minolta Spectrophotometer (model CM 3600d) connected to a computer was used to detect numerically the color coordinate values of the unaged leathers and artificially aged leathers. Colorimetric measurements were carried out on the leather samples. L* (lightness), a* (red-green color coordinate) and b* (yellow-blue color coordinate) color parameters were directly read using D65 illuminator and 10° standard observer (16).

The device was calibrated using a standard white plate before the measuring process. By means of a standard reading area with a diameter of 8 mm, 10 measurements for each

were taken. The averages of these measurements were also taken.

Statistical Analysis

Outputs were statistically analysed to find out the significant differences between the means of every aging steps of each aging procedure. For the stated purpose ANOVA, descriptive statistical test and Duncan test were carried out by using statistical software package (SPSS version 15.0). The 0.05 significant level was selected for the tests.

3. RESULTS AND DISCUSSION

3.1. Tensile strength and percentage extantion of artificially aged garment leather

One of the key elements that need to be taken into consideration in the determination of leather quality is tensile strength. Each change that occurs in leather fiber affects strength. Thus, by studying strength, it is possible to acquire reliable information about both the state and the usability of the leather (17). Any chemical degradation that occurs in leather structure negatively affects tensile strength and elongation (18).

The tensile strength of chrome-tanned garment leathers was found to be 15.28 N/mm² prior to ageing (Table 2). This value is in conformity with previous studies conducted on garment leathers and with acceptable quality standards for garment leathers (19-22). It was ascertained that the tensile strength values of Trial 5 among the leathers aged artificially by applying temperature factor and of Trial 5 and Trial 6 among the leathers aged artificially by applying temperature + UV ray and temperature + humidity factors were below acceptable quality standards (20,23).

Table 1. Experimental design of artificially aging process

ARTIFICIAL AGING FACTORS		
Temperature	Temperature + UV Ray	Temperature + Humidity
Control	Control	Control
Trial 1 24 h 50°C	Trial 1 24 h 50°C + UV	Trial 1 24 h 50°C + 90%
Trial 2 24 h 60°C	Trial 2 24 h 60°C + UV	Trial 2 24 h 60°C + 90%
Trial 3 72 h 60°C	Trial 3 72 h 60°C + UV	Trial 3 72 h 60°C + 90%
Trial 4 168 h 50°C	Trial 4 168 h 50°C + UV	Trial 4 168 h 50°C + 90%
Trial 5 168 h 70°C	Trial 5 168 h 70°C + UV	Trial 5 168 h 70°C + 90%

Table 2. Tensile strength results of chrome tanned garment leathers (N/mm²)

Leather Samples		Artificial Aging Factors		
		Temperature	Temperature + UV ray	Temperature + Humidity
Control	X±S.E.M.	15.28±0.003 ^{a,A}	15.28±0.003 ^{a,A}	15.28±0.003 ^{a,A}
Trial 1	X±S.E.M.	14.98±0.004 ^{a,B}	14.14±0.003 ^{c,B}	14.56±0.003 ^{b,B}
Trial 2	X±S.E.M.	13.77±0.006 ^{a,C}	13.20±0.004 ^{c,C}	13.35±0.004 ^{b,C}
Trial 3	X±S.E.M.	11.79±0.007 ^{a,D}	10.90±0.003 ^{c,D}	11.38±0.002 ^{b,D}
Trial 4	X±S.E.M.	10.46±0.003 ^{a,E}	9.13±0.005 ^{c,E}	9.93±0.004 ^{b,E}
Trial 5	X±S.E.M.	7.96±0.006 ^{a,F}	6.91±0.010 ^{c,F}	7.46±0.006 ^{b,F}

^{a, b, c} values in the same line with different superscript letters are significantly different (p<0.05).

^{A, B, C} values in the same column with different superscript letters are significantly different (p<0.05).

Table 3. Elongation results of chrome tanned garment leathers (%)

Leather Samples		Artificial Aging Factors		
		Temperature	Temperature + UV ray	Temperature + Humidity
Control	X±S.E.M.	78.33±0.667 ^{a,A}	78.33±0.667 ^{a,A}	78.33±0.667 ^{a,A}
Trial 1	X±S.E.M.	74.33±0.333 ^{a,B}	71.67±0.333 ^{c,B}	73.33±0.333 ^{b,B}
Trial 2	X±S.E.M.	68.67±0.882 ^{a,C}	65.00±0.577 ^{b,C}	67.33±0.333 ^{a,C}
Trial 3	X±S.E.M.	60.00±0.577 ^{a,D}	56.33±0.333 ^{c,D}	58.33±0.333 ^{b,D}
Trial 4	X±S.E.M.	50.00±0.577 ^{a,E}	47.00±0.577 ^{b,E}	48.33±0.333 ^{b,E}
Trial 5	X±S.E.M.	44.33±0.333 ^{a,F}	42.00±0.000 ^{b,F}	44.00±0.577 ^{a,F}

^{a, b, c} values in the same line with different superscript letters are significantly different (p<0.05).

^{A, B, C} values in the same column with different superscript letters are significantly different (p<0.05).

Table 4. Tear load results of chrome tanned garment leathers (N)

Leather Samples		Artificial Aging Factors		
		Temperature	Temperature + UV ray	Temperature + Humidity
Control	X±S.E.M. Thickness	37.49±0.004 ^{a,A}	37.49±0.004 ^{a,A}	37.49±0.004 ^{a,A}
		0.58 mm	0.58 mm	0.58 mm
Trial 1	X±S.E.M. Thickness	37.26±0.002 ^{a,B}	36.74±0.003 ^{c,B}	36.99±0.003 ^{b,B}
		0.48 mm	0.47 mm	0.55 mm
Trial 2	X±S.E.M. Thickness	36.14±0.002 ^{a,C}	35.29±0.003 ^{c,C}	35.75±0.004 ^{b,C}
		0.42 mm	0.46 mm	0.45 mm
Trial 3	X±S.E.M. Thickness	32.75±0.005 ^{a,D}	31.95±0.002 ^{c,D}	32.46±0.004 ^{b,D}
		0.51 mm	0.52 mm	0.55 mm
Trial 4	X±S.E.M. Thickness	30.58±0.002 ^{a,E}	29.87±0.003 ^{c,E}	30.15±0.004 ^{b,E}
		0.47 mm	0.50 mm	0.59 mm
Trial 5	X±S.E.M. Thickness	29.50±0.005 ^{a,F}	28.40±0.004 ^{c,F}	28.67±0.002 ^{b,F}
		0.56 mm	0.54 mm	0.55 mm

^{a, b, c} values in the same line with different superscript letters are significantly different (p<0.05).

^{A, B, C} values in the same column with different superscript letters are significantly different (p<0.05).

Another characteristic that should be considered in leathers processed for garment purposes is elongation because a low elongation value results in easy tear while a high elongation value causes leather goods to become deformed very quickly or even lose usability. If stretched under the influence of a force, leather, just like a wire, first gets thinner and then breaks. It is leather's elongation and in direct association with leather's fiber structure, orientation and fiber

direction. Furthermore, it is known that leather's fat content and humidity affect tensile strength and elongation.

As it can be seen in Table 3, the percentage extension value of the leathers included in the control group was determined to be 78.33%. However, maximum percentage extension is recommended to be 60% in acceptable quality standards for garment leathers (20,23). It was ascertained that the percentage

elongation value of each ageing factor decreased depending on time.

It was detected that the decrease observed in tensile strength and percentage elongation of each ageing factor depending on time was statistically significant (p<0.05). Besides, it was determined that the differences between the tensile strength value and the percentage elongation value of each ageing factor were significant at the level of $\alpha=0.05$ (Table 2 and Table 3).

3.2. Tear Load of artificially aged garment leather

Tear load is a characteristic that should be taken into account while determining the general strength characteristics of the fibres in leather's collagen tissue. The measure of leather's performance and strength during use is determined by means of tear load. However, not only the natural structure of leather but also the operations performed during leather processing are capable of affecting tear load negatively or positively.

The tear load of the chrome-tanned garment leathers subject to the research was ascertained to be 37.49 N before they were artificially aged by applying the ageing factors of temperature, temperature + UV ray and temperature + humidity. When Table 4 was analyzed, a time-dependant decrease was seen in the tear load values of the leather samples in each ageing factor. This decrease was determined to be statistically significant ($p < 0.05$). Besides, tear load differences between ageing factors were found to be statistically significant ($p < 0.05$). Even though a statistically significant decrease was detected between the tear load values before and after ageing, it was ascertained that the tear load values obtained were

in conformity with previous studies on garment leathers and with acceptable quality standards for garment leathers (20-22,24).

3.3. Shrinkage temperature of artificially aged garment leather

As a means of measuring collagen or leather stability and tannage in practice, shrinkage temperature is used by leather manufacturers and researchers. Raw, semi-processed and processed hides and skins used in the leather industry have unique shrinkage temperatures. Any modification made to collagen, which is the basic protein of leather, during leather production increases lateral cohesion force by increasing the number of cross links in collagen or creating additional cross links. Shrinkage temperature is also affected by such modifications (25).

In the shrinkage temperature test performed prior to ageing, the shrinkage temperature of the leathers subject to the research was found to be 120 °C (Table 5). It was ascertained that this value decreased up to 101 °C in the trials where only temperature factor was applied, up to 98 °C in the trials where temperature + UV ray factor was applied and up to 100 °C in the trials where temperature + humidity factor was applied. It was determined

that the time-dependant decrease observed in the shrinkage temperature values of each ageing factor was statistically significant and that the difference between the ageing factors of the shrinkage temperatures of other trial groups except for Trial 1 was statistically significant ($p < 0.05$).

The shrinkage temperature decrease observed in the collagen fibers of the research material leathers the shrinkage temperature of which was increased to 120 °C by being modified through tanning process indicates that the cross links between tanning agents and collagen started to partially rupture depending on ageing. This decrease observed in shrinkage temperature explains also the decreases in tensile strength and tear load values.

3.4. Color Evaluation of artificially aged garment leather

One of the most critical aspects of the marketability of a product is its color (26). Spectrophotometric techniques such as colorimetric color measurements are used to analytically evaluate color uniformity or stability of materials (27-30). Color quality is determined by the requirements of the end user thus, poor quality leather due to color defects is not acceptable (31,32).

Table 5. Shrinkage temperature results of chrome tanned garment leathers (°C)

Leather Samples	X±S.E.M.	Artificial Aging Factors		
		Temperature	Temperature + UV ray	Temperature + Humidity
Control	X±S.E.M.	120.00±0.000 ^{a,A}	120.00±0.000 ^{a,A}	120.00±0.000 ^{a,A}
Trial 1	X±S.E.M.	118.00±0.000 ^{a,B}	116.00±0.000 ^{a,B}	117.00±0.000 ^{a,B}
Trial 2	X±S.E.M.	114.33±0.167 ^{a,C}	111.50±0.000 ^{c,C}	113.16±0.167 ^{b,C}
Trial 3	X±S.E.M.	109.00±0.000 ^{a,D}	107.16±0.167 ^{c,D}	108.00±0.000 ^{b,D}
Trial 4	X±S.E.M.	105.00±0.000 ^{a,E}	102.66±0.333 ^{c,E}	104.00±0.000 ^{b,E}
Trial 5	X±S.E.M.	101.00±0.000 ^{a,F}	98.00±0.000 ^{c,F}	100.00±0.000 ^{b,F}

^{a, b, c} values in the same line with different superscript letters are significantly different ($p < 0.05$).

^{A, B, C} values in the same column with different superscript letters are significantly different ($p < 0.05$).

Table 6. Lightness values of chrome tanned garment leathers (L*)

Leather Samples	X±S.E.M.	Artificial Aging Factors		
		Temperature	Temperature + UV ray	Temperature + Humidity
Control	X±S.E.M.	24.38±0.224 ^{a,A,B}	24.38±0.224 ^{a,B}	24.38±0.224 ^{a,D}
Trial 1	X±S.E.M.	23.88±0.075 ^{b,B}	23.76±0.012 ^{b,C}	24.69±0.402 ^{a,b,C,D}
Trial 2	X±S.E.M.	24.51±0.107 ^{b,A}	25.47±0.172 ^{a,A}	25.81±0.020 ^{a,B}
Trial 3	X±S.E.M.	24.82±0.306 ^{b,A}	25.50±0.165 ^{a,A}	25.85±0.029 ^{a,B}
Trial 4	X±S.E.M.	24.74±0.100 ^{c,A}	25.59±0.081 ^{b,A}	26.63±0.294 ^{a,A}
Trial 5	X±S.E.M.	24.55±0.067 ^{c,A}	25.16±0.026 ^{b,A}	25.35±0.051 ^{a,B,C}

^{a, b, c} values in the same line with different superscript letters are significantly different ($p < 0.05$).

^{A, B, C} values in the same column with different superscript letters are significantly different ($p < 0.05$).

When the L* (lightness) values of the chrome-tanned garment leathers as research materials were analyzed, it was understood that the L* (lightness) values of Trial 1 decreased slightly compared to the control group in each ageing factor, in other words, the color became slightly darker but this

darkening was not statistically significant except for the artificial ageing conducted by applying temperature + UV ray ($p > 0.05$) (Table 6). Starting from Trial 2, a general increase was seen in the L* (lightness) value of all ageing factors. It was ascertained that this increase seen in

ageing factors was statistically significant except for the artificial ageing conducted by applying temperature factor ($p < 0.05$). Increase in L* (lightness) value means lightening (16,28,32).

Table 7. Red-green color coordinate values of chrome tanned garment leathers (a*)

Leather Samples	X±S.E.M.	Artificial Aging Factors		
		Temperature	Temperature + UV ray	Temperature + Humidity
Control	X±S.E.M.	0.85±0.023 ^{a,A}	0.85±0.023 ^{a,A}	0.85±0.023 ^{a,A}
Trial 1	X±S.E.M.	0.64±0.025 ^{a,B}	0.61±0.023 ^{a,B}	0.48±0.031 ^{b,B}
Trial 2	X±S.E.M.	0.54±0.023 ^{a,C,D}	0.43±0.024 ^{b,C,D}	0.32±0.029 ^{c,D}
Trial 3	X±S.E.M.	0.57±0.029 ^{a,B,C}	0.48±0.017 ^{b,C}	0.39±0.021 ^{c,C,D}
Trial 4	X±S.E.M.	0.59±0.024 ^{a,B,C}	0.56±0.032 ^{a,B}	0.44±0.035 ^{b,B,C}
Trial 5	X±S.E.M.	0.48±0.015 ^{a,D}	0.39±0.027 ^{b,D}	0.33±0.012 ^{b,D}

^{a, b, c} values in the same line with different superscript letters are significantly different ($p < 0.05$).

^{A, B, C} values in the same column with different superscript letters are significantly different ($p < 0.05$).

Table 8. Yellow-blue color coordinate values of chrome tanned garment leathers (b*)

Leather Samples	X±S.E.M.	Artificial Aging Factors		
		Temperature	Temperature + UV ray	Temperature + Humidity
Control	X±S.E.M.	-0.11±0.023 ^{a,A}	-0.11±0.023 ^{a,A}	-0.11±0.023 ^{a,A}
Trial 1	X±S.E.M.	-0.34±0.045 ^{a,B,C}	-0.42±0.007 ^{a,B,C}	-0.33±0.052 ^{a,B}
Trial 2	X±S.E.M.	-0.34±0.012 ^{b,B,C}	-0.40±0.057 ^{b,B,C}	-0.15±0.015 ^{a,A}
Trial 3	X±S.E.M.	-0.26±0.077 ^{b,C,B}	-0.29±0.067 ^{c,B}	-0.08±0.017 ^{a,A}
Trial 4	X±S.E.M.	-0.32±0.018 ^{a,B,C}	-0.39±0.104 ^{a,B,C}	-0.31±0.026 ^{a,B}
Trial 5	X±S.E.M.	-0.42±0.049 ^{b,C}	-0.57±0.015 ^{c,C}	-0.26±0.030 ^{a,B}

^{a, b, c} values in the same line with different superscript letters are significantly different ($p < 0.05$).

^{A, B, C} values in the same column with different superscript letters are significantly different ($p < 0.05$).

On the other hand, depending on the changes in a* and b* values, it is possible to determine the color differences on a leather surface. Higher values of a* and b* define a fading of the color. As seen in Table 7 and Table 8, a* and b* values in the Trials of artificially aged garment leathers were higher than control groups.

4. CONCLUSION

As a conclusion, decrease in the tensile strength and tear load, fall in the shrinkage temperature and fading in the color of the artificially aged chrome-tanned garment leathers by applying the ageing factors of

temperature, temperature + UV ray and temperature + humidity were ascertained. Moreover, it was found out that the artificial ageing factors of temperature + UV ray, temperature and temperature + humidity (respectively according to their level of influence) caused significant losses of quality on garment leathers.

Within the scope of these results, it is possible to state that leather's natural ageing process can not be prevented but can be slowed down by taking ageing-causing factors under control. Therefore, attention should be paid to ambient temperature, humidity and sunlight at leather and leather products storage, production and sales stages.

If attention is paid to these matters, leather garments are protected from being deformed in a short time and completing their economic life earlier and thus contribution can be made to consumers' budget and to the national economy.

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