Effects of Atmospheric Pressure Plasma Treatments on Various Properties of Leathers

by

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Abstract

Chrome tanned crust leathers were treated with atmospheric pressure plasma with argon flows at different times. The leather was then dyed with acid and metal complex dyes. The dyestuff concentration in the exhausted dye bath, CIE lab color analysis, hydrophilicity, FTIR spectra and SEM images were compared for 0, 2.1, 4.2 and 6.4 sec/cm^2 durations of plasma. In addition, various physical properties such as rubbing fastness, tear loading and tensile strength were also examined to see the effects of increased duration of the plasma process. The presence of ions that appeared during this process in an atmospheric environment was determined by OES. The best results were obtained from leather subjected to 6.4 sec/cm^2 of argon gas atmospheric pressure plasma.

Resumen

Crosta de cueros al cromo fueron tratados por medio de plasma a presión atmosférica en flujos con Argón durante diferentes tiempos. El cuero luego fue teñido con colorantes aniónicos así como también complejos metálicos. La concentración del colorante en los baños agotados, CIE lab color analysis de Hunter Laboratories, Hidrofilicidad, Espectroscopia IR. Fourrier, e imágenes electro microscópicas por barrido electrónico, fueron comparadas a 0, 2.1,4,2 y 6,4 seg/cm^2 de tiempos de aplicación del plasma. En adición ciertas propiedades físicas como resistencia al frote, carga al momento de rotura, resistencia a la rotura, fueron examinadas para determinar los efectos del tiempo cuando el cuero fue sometido a la acción del plasma. La presencia de iones resultantes del Argón a presión atmosférica fueron determinados por OES. Los mejores resultados fueron obtenidos en cuero sometido 6,4 seg/cm^2 tiempo de contacto con el plasma de argón a presión atmosférica.

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Introduction

The leather industry has to produce leather that is appropriate in color, pattern and quality for seasonal trends, and in accordance with changing fashions and demands. Dyeing is a key process because it gives the leather the desired color and appeal.[1] In the dyeing of leather, acid and metal complex dyestuffs are often used.[2] However, dyestuff that has not been bound to the leather is released to the environment with waste water in the dye bath at the end of the dyeing process. Dyeing waste water can be decolorized with different chemical substances and biotechnological applications,[3, 4] but the compounds that provide the color are complex structures, and this can make the decolorization process difficult. Also, the resulting by-products can sometimes be more harmful and toxic than the initial compounds.[4, 5]

For this reason, emphasis has been put in recent years on work to reduce the release of waste water containing dyestuff by using different methods in the dyeing process or different auxiliary dyeing materials.[6, 7] The desired dye shade can be obtained more easily by ensuring the bonding of a dyestuff that did not previously bind to the leather in the dye bath. In this way, there will be a reduction in the amount of dyestuff used in top dyeing or the need for top dyeing will be eliminated.[8]

Plasma technology is a new technology which is being used in many areas today, principally in medicine, chemistry, the textile industry, waste water treatment systems and biology.[9] Plasma is called fourth state of matter, and requires energy for its formation. A plasma contains ions, electrons, photons, excited atoms or molecules, radicals, and metastable atoms, neutral atoms or molecules. Plasma treatment on the surface of a material can make various modifications in the form of surface activation, etching, grafting and cross-linking, deposition.[10, 11] Plasma technology has various advantages: for example, it does not need water; the process occurs in the gas phase, the amount of chemicals used is reduced, it does not cause industrial waste, and the process makes modifications to the surface of the material without disturbing its basic properties.[12]

The aim of this study was to give a surface activation feature to the chrome tanned crust leather by plasma application and increase the dye uptake of the leather by increasing its hydrophilicity. The leathers were subjected to atmospheric pressure plasma with argon gas for different durations of time under constant power and gas flow. Following the plasma process, the leathers were subjected to a dyeing process with acid and 1:1 metal complex dyes. At the end of the dyeing process, the dye concentration in the exhausted dye bath, dyeing fastness, and certain characteristics of the leathers were determined.

Materials and Methods

Material

Twelve pickled sheep skins of Turkish origin were used in the study. Sheep skins were obtained from Menemen Leather Industrial Area in Izmir.The acidic protease used was Oropon DVP (TFL *Leather Technology* Ltd.), the degreasing agent used was Rinolen 3000 S (Deteks Chemicals), basic chrome sulphate (basicity 33%) used was Tankrom AB (Soda Sanayi A.S.), the sulphited deodorized fish oil used was Fosfol Al-30 (Cromogenia-Units S.A.), the sulphited natural oil based fatliquor used was Sulphirol VV 60 (Smit and Zoon), the lecithin-based fatliquor used was Fosfol LP (Cromogenia-Units S.A.), the combination of synthetics and sulphated esters oils used was Fosfol 51 (Cromogenia-Units S.A.), the combination of sulphochlorinated synthetic parafin and emulgators used was Alpine Soft SCP (Alpine Chemicals), the acid dyestuff used was Coriacido Black T (Stahl holdings b.v.) and the metal complex dyestuff used was Base Black NA (Stahl holdings b.v.). Sodium formate and formic acid were supplied by BASF-The Chemical Company and sodium bicarbonate was supplied by Soda Sanayi A.S.

Method

Leather Processing

Skins were tanned with basic chrome sulphate according to traditional methods, they were left to crust. The recipe for the chrome tanning and the post tanning process of the skins recipe is given in Table I. Later, 10x14 cm samples were cut from the sampling areas of the leathers for plasma application.

Experimental Set Up

Plasma treatment of the leather samples was performed with an atmospheric pressure plasma device of laboratory scale that produces plasma of the corona discharge type at radio frequency (Figure 1). The physical parameters such as power supply, nozzle's diameter, and distance of electrodes were optimized. The optimized plasma parameters were at a frequency of 5.4 kHz, 21.5 Watts power, a voltage of 16 kV and 13.5 mA of current. A copper electrode of length 10 cm and diameter 2.6 mm was placed in the center of the nozzle and the distance from the tip of the nozzle to the leather was set to 11 mm. The nozzle had an internal diameter of 10 mm, a length of 13 cm, a thickness of 1.9 mm and the internal diameter of the glass at the mouth of the nozzle was 6 mm.

After the parameters of the plasma had been set, argon gas was applied to the leathers at a flow rate of 11.65 l/min for 0 sec/cm^2 in group 1, 2.14 sec/cm^2 in group 2, 4.28 sec/cm^2 in group 3 and 6.42 sec/cm^2 in group 4 in order to see the effects of the plasma over time.

TABLE I
Recipe used on the skins.

	Chemical Additives	Temperature (ºC)	Proportion (%)	Time (min)	Remarks
Weighing					Total Weight= skin weight + 40% of skin weight
Depickle	Water	26	200		
	Common salt			20	7ºBé
	Sodium formate		1	30	
	Sodium bicarbonate		1	45	pH: 5.2, drain
Washing	Water	26	300	15	Drain, pre-fleshing
Washing	Water	26	300	15	Drain
Bating	Water	32	100		
	Oropon DVP		2	30	Drain
Washing	Water	26	300	15	Drain
Degreasing	Rinolen 3000 S		4	60	
Washing	Water	35	300	20	Twice, drain
Pickle	Water	26	100		
	Common salt			20	7ºBé
	HCOOH		0.5	30	
	H_2SO_4		1	60	pH:2.8
Tanning	Tankrom AB		8	240	
Basification	Sodium formate		1	30	
	Sodium bicarbonate		0.5	45	pH:3.9, drain
Washing	Water	26	300	15	Drain, 48 h horse up
Washing	Water		300	10	
Neutralization	Water	35	250		
	Sodium formate		1	30	
	Sodium bicarbonate		1	45	
Washing	Water	26	300	10	
Fatliquoring	Water	35	100		

Table I continued on the following page.

Table I continued.

	Chemical Additives	Temperature (°C)	Proportion (%)	Time (min)	Remarks
	Fosfol AL-30		1		
	Sulphirol VV 60		1		
	Fosfol LP		2		
	Fosfol 51		1		
	Alpine Soft SCP)		1	60	
	Formic Acid		1	30	
Washing	Water		300	15	
Drying, process mechanics and plasma application					
Weighing					
Dyeing	Water	45	200		
	Sodium formate		1	30	
	Dyestuff		4	30	Metal complex dye or acid dye
	Formic acid		2	20	pH: 4.0, drain

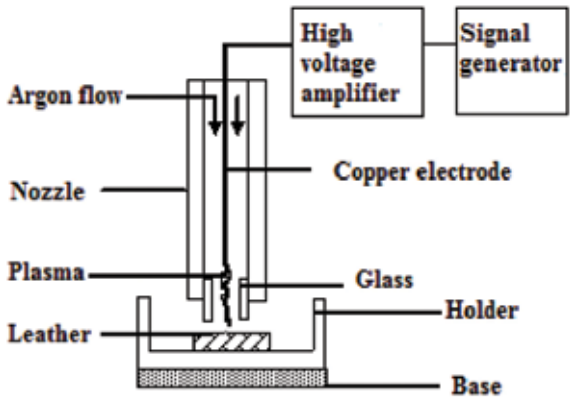


Figure 1. Schematic View of Atmospheric Pressure Plasma Apparatus.

The Dyeing Process

Leather samples treated with plasma for different durations of time were taken for the dyeing process with an acid dye material of Color Index Number Acid Black 210, and 1:1 metal complex dye material of Color Index Number Acid Black 172. The dyeing recipe after plasma application is given in Table I.

Optical Emission Spectrometer Analysis

Optical emission spectrometer (OES) is a frequently-used method for monitoring and identifying optical radiation emitted by the plasma. The Optical Emission Spectrum shows the types of neutral particles and ions in the plasma by measuring the wavelengths and intensities of the series. In this way, information about the physical phenomena occurring in the plasma can be obtained with OES analysis.[13] The optical cable of the OES monochromator was placed on the tip of the atmospheric pressure plasma nozzle and the results were analyzed in the OES.

FTIR Measurements

FTIR analysis was conducted in order to determine the differences in the chemical properties of leather treated with plasma for different durations of time and leather that had not been treated. FTIR studies were conducted on a Perkin-Elmer Spectrum 100 device with ATR equipment. For this purpose, the leather samples were scanned with IR spectrums at a wavelength of 4000-400 cm^{-1} and the results were evaluated in the FTIR Spectrum Software (Perkin Elmer) and compared with the spectrums in the literature.

Hydrophilicity Measurements
The leathers were conditioned under standard atmospheric conditions as recommended in IUP 1 and IUP 3 at a temperature of 23°C ± 2°C and 50% ± 5% relative humidity, and the sampling location was determined according to IUP 2. Wettability of the leather samples was characterized by the water droplet test (IUP/420). Five readings were taken from different parts of the treated and untreated leather samples.[14, 15, 16, 17]

Dyestuff Concentration in the Exhausted Dye Bath
The dyestuff concentration in the process liquor was analyzed using a Shimadzu UV–Visible 1601 spectrophotometer. The percentage of dyestuff concentration (DC) was calculated using the following equation:

$$\% \text{ DC} = [(C_r - C_t)/ C_r] \times 100$$

where C_r and C_t represent the amount of dyes at the end of dyeing procedure for the reference and treated samples respectively.[18]

This was carried out using Helma brand quartz cuvettes of 1x1x4 cm dimensions in the UV-visible spectrophotometer (Varian Cary 300 Bio). The measurements were carried out at the wavelengths at which the dyes gave the maximum absorbance values. These wavelengths were determined to be 465 nm for the acid dye and 575 nm for the metal complex dye.

CIE L^* a^* b^* Color Measurement
A Konica Minolta CM-508D brand global spectrophotometer with an 8 mm diameter measurement area was used in the measurement of the leather dyes. Measurements were taken from 10 different areas of each leathers according to CIE Lab (1976) and the color differences were determined between treated and untreated leathers.[19] In the components of the CIE Lab color space, L* is the lightness of color, and a* and b* indicate the color. If L* has a negative value, it means that the color of sample has darkened, while if it has a positive value, it means that the sample color has turned lighter. If a* has a negative, it means that the sample color has turned greener, and if it has a positive value, it means that the sample color has turned redder. If b* has a negative value, it means that the sample color has become bluer, and if it is positive, it means that the sample color has turned yellower.[20, 21]

Rubbing Fastness
Leathers were conditioned under standard atmospheric conditions as recommended in IUP 1 and IUP 3 at a temperature of 23°C ± 2°C and 50% ± 5% relative humidity, and sampling locations were determined according to IUP 2.[14, 15, 16] The rubbing fastness (dry and wet) of the dyed samples was measured according to IUF/450 using Otto Specht Bally Finish Tester 9029. Changes in the color of the leather and the felt were measured using a grey scale according to ISO 105-A02 and ISO 105-A03.[22]

Tensile Strength and Tear Load Tests
Leathers were conditioned under standard atmospheric conditions as recommended in IUP 1 and IUP 3 at a temperature of 23°C ± 2°C and 50% ± 5% relative humidity, and sampling locations were determined according to IUP 2.[14, 15, 16] The tensile strength of the dyed samples and the tear load of the dyed samples were measured according to IUP/6 and IUP/8 respectively, using Shimadzu AG-IS Test Apparatus.[23, 24]

Scanning Electron Microscope Study
The samples were placed on a scanning electron microscope (Philips XL-30S FEG) and their images were taken at x100 magnification.

RESULTS AND DISCUSSION

Optical Emission Spectrometer
The OES graph used for the detection of gases in the environment during the argon plasma process is shown in Figure 2.

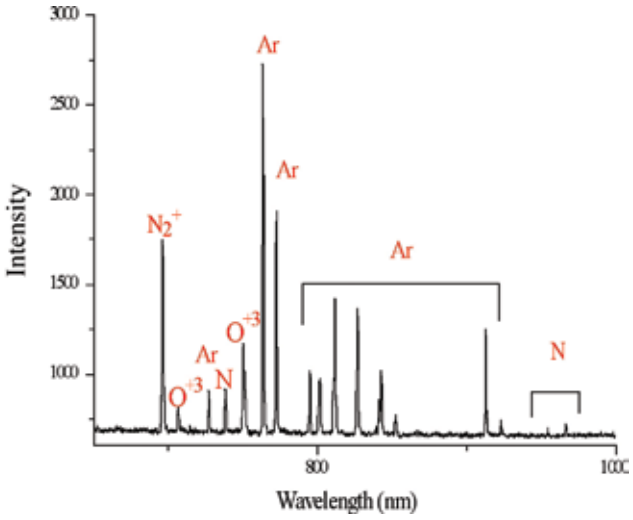


Figure 2. OES Image during Ionization with the Argon Plasma Process.

Since the plasma process was carried out at atmospheric pressure, gases in the atmosphere other than argon affected the process. When Figure 2 is examined, it can be seen that although there was mostly argon gas in the environment, O^{+3}, N and N_2^+ gases also ionized during the plasma process. In plasma applications containing argon gas at atmospheric pressure, impurities like N_2, OH, O^{+3}or O_2 can affect the process and this is known as emission operation cycle air leakage. The impact intensity of the newly formed gases differs depending on the light source used and other sources of excitation.[23, 25] In other studies, the effects of the plasma process occurred together with synergic effects of the gas used during the plasma process and other atoms present in the

environment. In addition, free radicals like peroxide or new groups that can form new bonds (C=O, OH) sometimes occur, and these new bonds occur depending on the material used.[26, 27, 28]

FTIR

The FTIR spectrum for crust leathers groups 1, 2, 3 and 4 treated with argon plasma are given in Figure 3. Leather consisting of Type I collagen-based protein was designated as peptide groups Amide A, B, I, II, III, VII when examined in FTIR.[29]

Generally the Amide A band gives a peak depending on the N-H stretching frequencies. Although the free N-H tension vibration occurs in the 3400- 3440 cm^{-1} range, when the N-H group is bound to a peptide chain containing hydrogen bonds, the vibration position shifts towards a lower frequency of about 3300 cm^{-1}.[30, 31] The peak interval of 3291 cm^{-1} in Figure 3 has been associated with this shift. Amide B on the other hand consists of asymmetric CH_2 groups and occurs in the range between 3100 and 2900 cm^{-1}. When Figure 3 is examined, it can be seen that the peak it gives at 2921 cm^{-1} is associated with Amide B.[31, 32] The Amide I group that has the most intensive absorption band among the proteins has peak intervals of 1600 and 1700 cm^{-1} with the vibration of C = O (70-85%), and C-N groups (10-20%).[29, 30] The peaks of 1735 and 1647 cm^{-1} that occur in Figure 3 represent the Amide I groups. The Amide II group is comprised of a mixture of N-H (40-60%) C-N (18-40%) and C-C (10%) groups and has a more complex structure than Amide I, which gives a peak at 1510 and 1580 cm^{-1}. Therefore, the 1548 cm^{-1} peak occurring in FTIR is associated with Amide II. The Amide groups III and V are comprised of even more complex structures, and are especially sensitive to changes in proteins due to denaturation; the peaks between 1230 and 1250 cm^{-1} are associated with Amide III groups. The 1256 and 1233 cm^{-1} peaks occurring in the FTIR spectrum have been associated in this way.[29, 33] The 517 and 621 cm^{-1} peaks in the FTIR spectrum are attributed to the deformation modes of the metal-oxygen chain. Because chrome was used in the tanning process, the 673 cm^{-1} peak occurring in the FTIR spectrum is associated with the Cr_2O_3 in the leather.[34, 35] Due to both the raw leather containing natural fat acids and fat-liquoring substances being used during the processing of the leather, the crust leathers gave a peak at 1448 cm^{-1} in the FTIR spectrum. All of these peaks are characteristic peaks naturally present in the leather.[36] However, a decrease was observed in the spectrum at the 2852 and 2920 cm^{-1} peaks due to an increase in plasma duration. This is due to methylene and methyl groups breaking from the surface of the molecule in the next chain with increased plasma optimization, and the separation of a carbon atom with three bonds.[37] In addition, the peaks between 2359 and 2342 cm^{-1} that occurred in the leather subjected to plasma containing 6.42 sec/cm^2 argon were associated with an increase of alkyl groups on the surface.[37]

Hydrophilicity

Water droplet results are listed in Table II. The decrease in the leathers' water droplet absorption time with an increase in the plasma period applied to the leathers shows that the hydrophilicity of the leathers improved. When our findings were compared with other studies, similar results were seen to have been obtained. In a study by Choi et al. (2003), it was

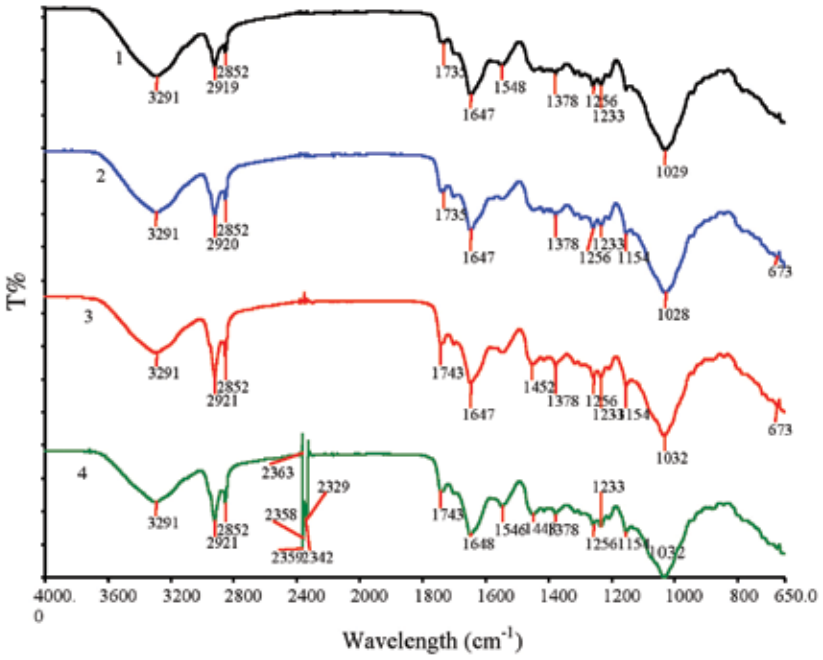


Figure 3. FTIR Spectra of Plasma-treated Leathers.

TABLE II
Results for hydrophilicity of leathers and dyestuffs concentration in the exhausted dye bath.

Groups	Hydrophilicity (sec) Mean±SD	Concentration of metal complex dye (ppm) Mean±SD	Concentration of acid dye (ppm) Mean±SD
1	162±2.1	29±1.2	64±1.3
2	82±1.9	20±1.4	48±1.2
3	64±1.6	16±1.1	40±1.3
4	44±1.2	14±1.0	33±1.1

reported that the hydrophilicity of the leather is caused by an oxygen atom that is separated when the plasma oxidizes after being absorbed by the leather's surface.[38] Ozdogan et al. (2011) reported that the hydrophilicity of leather samples was increased by atmospheric pressure argon plasma application because of increase of groups containing oxygen (-OH, C=O, -COOH) on the leather surface.[39]

Dyestuff Concentration in the Exhausted Dye Bath

Plasma processes using argon gas increase dyeability with acid dyestuff, and higher dye fixation provides faster and more uniform dye uptake.[40] In plasma applications performed in an atmospheric environment, gases like oxygen and nitrogen can affect the system and contribute to the effects created by the plasma application. Similar results were obtained in our research, where atmospheric plasma application using argon gas decreased the dyestuff concentration in the exhausted dye bath (Table II). It was determined that the increase in dye consumption increased along with an increase in the duration of plasma application. In leathers dyed with both metal complex dye and acid dye, the lowest concentration values (20 ppm and 48 ppm respectively) were given by group 1 leathers treated with 2.14 sec/cm^2 plasma, while the best concentration values (14 ppm and 33 ppm respectively) were obtained from group 4 leathers treated with 6.42 sec/cm^2 plasma.

CIE L* A* B* Color

The spectrophotometric color values of leather samples dyed with metal complex and acid dyestuff after being exposed to plasma are given in Table III. It was established that the L value of leathers dyed with both metal complex and acid dyestuff decreased with an increase in plasma treatment duration. When the a value was assessed, it was found that the redness of the leathers increased parallel to increased plasma treatment duration in plasma treated leathers dyed with both metal complex and acid dyestuff. When the b color values of the leathers were examined, it was determined that in leathers dyed with metal complex dyestuff, the value was negative including the control group, and that it increased with increasing plasma treatment durations. However, the b value in leathers dyed with acid dye was seen to be positive even in the control group. This means that there was a decrease in the blueness of the leathers with the increase in plasma treatment durations.[41]

Rubbing Fastness

The wet and dry rubbing fastness of the leathers is shown in Table IV. The rubbing fastness of the leathers in our study dyed with metal complex and acid dyestuff improved in parallel with an increase in plasma treatment duration. In the wet and dry rubbing fastness of the leathers, group 4 leathers to which 6.42 sec/cm^2 plasma was applied showed the best values. An increase in the wet and dry rubbing fastness of the leathers was obtained with an increase in plasma treatment duration. When the wet and dry rubbing fastnesses of the leathers were compared, a slight difference was seen between the wet rubbing fastness and the dry rubbing fastness of the leathers.

Tensile Strength and Tear Load Assessment

The physical characteristics of leathers are important in terms of preparing the desired final leather goods.[42] Therefore, information about the condition of the finished leather and its usability can be obtained by examining its tensile strength. The findings regarding the tensile strength and tear load assessment of leathers in our study are given in Table IV. A good tensile strength value is generally a feature to be desired for all types of leather and is a good indicator of the quality of the leather.[43] UNIDO has stated that the tensile strength value of chrome tanned clothing leather should be at least 10 N/mm^2.[44] BASF stated that the tensile strength value of clothing leather should be at least 12 N/mm^2.[45] Our studies showed that while the tensile strength of leather dyed with metal complex dyestuff varied between 12.96 N/mm^2 and 14.62 N/mm^2, it was between 13.01 N/mm^2 and 17.58 N/mm^2 in leather dyed with acid dyestuff. The lowest tensile strength values for both dyestuffs were observed in group 4 leathers subjected to the

TABLE III
L^*, a^*, b^* results.

Groups	L*	a*	b*
Metal complex dye	Mean±SD	Mean±SD	Mean±SD
1	24.71±1.78	1.37±0.18	-2.28±0.19
2	23.05±1.41	1.38±0.17	-1.67±0.27
3	22.95±1.60	1.42±0.15	-1.57±0.25
4	21.52±1.69	1.46±0.18	-1.24±0.17
Acid dye			
1	32.36±1.98	1.05±0.12	1.49±0.11
2	31.08±1.82	1.08±0.13	1.48±0.24
3	30.63±2.03	1.14±0.11	1.35±0.34
4	29.30±1.84	1.23±0.13	1.23±0.13

TABLE IV
Rubbing fastness, tensile strength and tear load results.

Groups	Dry rubbing		Wet rubbing		Tensile strength	Tear load
	Leather	Pad	Leather	Pad	N/mm^2	N/mm
Metal complex dye					Mean±SD	Mean±SD
1	4	4	4/5	4	14.62±0.11	11.44±0.55
2	4	4/5	5	4	13.91±0.23	10.83±0.10
3	4/5	4/5	5	4/5	12.96±0.14	10.69±0.37
4	5	5	5	5	13.61±0.15	10.45±0.42
Acid dye						
1	5	4/5	4/5	3/4	17.58±0.96	8.08±0.23
2	5	4/5	4/5	3/4	15.12±0.11	7.16±0.18
3	5	4/5	5	4	14.26±0.47	7.08±0.32
4	5	5	5	5	13.01±0.36	7.06±0.54

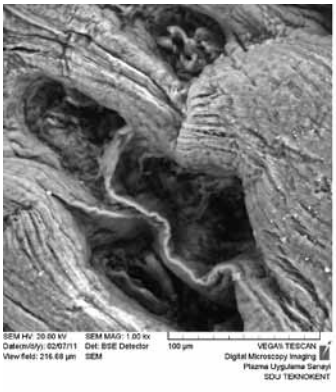
6.42 sec/cm^2 plasma application. Reduced tensile strength was determined with increased plasma treatment duration.

When the tear load test results given in Table IV were examined, it was found that group 1 leathers dyed with acid dyestuff and not treated with plasma had a strength of 8.08 N/mm, while leathers dyed with metal complex dyestuff gave the highest tensile strength value of 11.44 N/mm. The lowest values obtained for both dyestuffs were 7.06 N/mm and 10.45 N/mm respectively for group 4 leathers with 6.42 sec/cm^2 plasma applied. A reduced tear load value was determined with the increase in plasma duration, and the same was true with tensile strength. While UNIDO stated that the double side tearing values of chrome tanned clothing leathers should be 15 N/mm, BASF stated that the double side tearing value of clothing leather should be at least 20 N/mm.[44, 45]

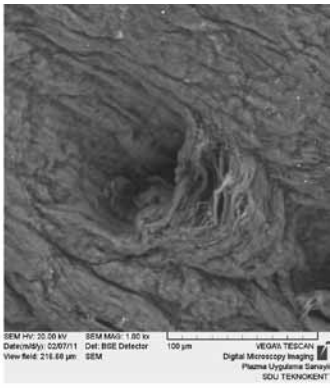
All tensile strength values and tear load values in our study were below the above-mentioned standards. Modification of the fibrous structure making up the collagen network has an effect on the strength values of the leathers.[46] It is thought that the decrease in strength values of the leathers arose from damage to the leather fibers during the application of the plasma process.[47] One other reason why these values were low is that in order to see the effects of the plasma, the leather samples were not modified until they had reached their final condition.

SEM Photographs

SEM images 100 x magnification of crust leather subjected to the plasma process using argon for varying durations are given in Figure 4. These images show that deformations on the surfaces of the leathers increased as the duration of the plasma application increased.[48] The results of our studies were seen to agree with the results of Osin et al. (1998)'s work.



Group 1



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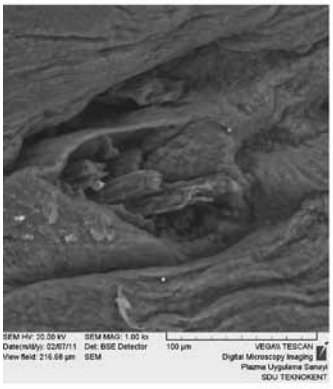

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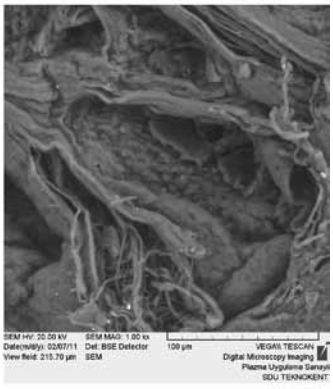

Group 4

Figure 4. SEM Images of Plasma-Treated Crust Leathers.

CONCLUSIONS

The application of atmospheric pressure argon plasma improved the surface properties of chromium-tanned leather. The plasma process improved color intensity leveling with an increased hydrophilicity effect on the surfaces of crust leathers and an increase in the capacity of the leather to form chemical bonds. Based on these results, plasma technology not only gives functional properties to leather, but also presents alternative possibilities for the leather production process. It is thought that, if different gas combinations and different plasma techniques are used, and if the system is designed appropriately for leather processing and surface applications, the sector can fulfill the expectations of better dyeing properties and environmentally friendly leather processing. However the study found that the physical properties of leather samples significantly decreased as the duration of plasma application increased. For this reason, the plasma duration needs to be reduced as much as possible in the atmospheric pressure plasma application of leather.

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