INDUSTRIAL TRIALS FOR A MORE ECOLOGICAL CHROMIUM TANNING

HASAN ÖZGÜNAY[1], MEHMET METE MUTLU[1], CEMILE CEREN TOSUN[2], ÖZGÜR DEMIRCI[2], ONUR ABALI[2], YIGIT KAMAN[2], TALIP SEPICI[2]

[1]*Ege University, Engineering Faculty, Faculty of Leather Engineering, Bornova, İzmir, Turkiye, Phone: +90 232 311 26 44, e-mail: hasan.ozgunay@ege.edu.tr*

[2]*Sepiciler Caybasi Leather Company, Mustafa Kemal Atatürk Mah. Izmir - Aydın Asfalti Cad. No: 110 Torbalı - Izmir 35860, Turkiye, Phone: +90 232 850 50 00 e-mail: cemile.tosun@sepici.com.tr*

In leather production the chrome tanning method is the most widely used tanning system all over the world despite the storage and disposal of solid wastes and sludge containing high amounts of chromium poses a major challenge. For this reason many researches based on higher exhausting and lower chromium used technologies have emerged in the recent past. However, these technologies are not directly accepted by the industry due to risks and some possible changes in quality issues. Accordingly, in this project one of these approaches: chromium tanning without pickling process, using less chromium salts at higher initial pH is tried in pilot scale at a leading company in Turkish leather industry. The variables used in the research were; pre-tanning agents (aldehyde, sulphonyl chloride, and synthetic tanning agent), initial pH of tanning (5.0-5.5 and 6.0-6.5) and tanning agents (standard basic chromium sulphate and commercial tanning agent with lower chromium oxide content). The wet-end processes and finishing processes of the leathers were applied according to the company's production line. Chromium content of the leathers and the Cr_2O_3 remaining in effluents were determined for each tanning application. Also, the physical properties of the leathers were investigated. The Cr_2O_3 of the leathers were found to be varying between 3.12-4.83% while the remaining chromium in the effluents was between 16.9 - 1347 mg/L. Additionally, the properties of the final leathers were evaluated comparatively with company's regular products, considering the test results and organoleptical evaluations it was concluded that many of them were comparable to conventional chromium tanned regular products.

Keywords: Leather, Chromium Tannage, High Exhaustion

INTRODUCTION

Conventional chromium tanning process which is used for approx. 80% of produced leathers consists of three main steps namely pickling, tanning, and basification. Pickling; is being performed along with brine solutions and acids and tanning is being carried out by using 8-10% of basic chromium sulphate over pelt weight. Then, in basification step reactivity of chromium is increased and fixation is achieved by introduction of alkali salts. Since whole of the chromium used in process cannot be exhausted, approx. 1/3-1/4 of it (1500 – 5500 mg/L) remains in bath at the end of the process (R&D Dept Seta, Brazil, 2000; Sreeram *et al*., 2006; Tao *et al*., 2014). Treatment, storage and disposal of this this chromium containing effluents and sludge poses a major challenge. There are various approaches i.e. ameliorating the parameters of chrome tanning, modifying chrome tanning agents or the collagen and using auxiliary agents and/or combination tanning agents towards preventing these technical and environmental problems caused by conventional chromium tanning (Morera *et al*., 2006; Luan *et al*., 2007; Luo *et al*., 2009; Sundar *et al*., 2007; Thanikaivelan *et al*., 2002). Among these alternatives, higher exhausting chromium tanning technology applied at higher initial pH values without pickling by lower chromium offer is a promising one in recent years.

However this technology is not directly switched to application in the industry due to potential risks like incomplete penetration and precipitation of chromium on the leather surface due to high initial pH values and possible quality variations in the final products. In the present research adopting of higher exhausting ecological chromium technology instead of existing conventional chromium tanning is investigated in pilot scale at a leading company in Turkish leather industry by designing various experiments to optimize the process and to maintain similar properties and quality from the produced leathers.

MATERIAL AND METHODS

Lime split domestic pelts (to be approx. 50 kg per each trial) which were conventionally processed were used as material. They were delimed and bated according to company's production route. As blank, the first trial was performed according to company's conventional chromium tanning system with pickling. Other trials were performed without pickling and the necessary pH values depending on the pre-tanning agents were adjusted by using non-swelling acids. An aldehyde, a sulphonylchloride and a highly reactive syntan which are available in the market were selected to be used as pre-tanning agents. After pre-tanning stage, the pH of the pelts were adjusted to 5-5.5 and 6-6.5 respectively and chromium tanning was performed by using 5% standard basic chromium sulphate and 6% of a commercial chromium tanning agent having lower basicity and Cr_2O_3. The trial scheme is given in Fig.1.

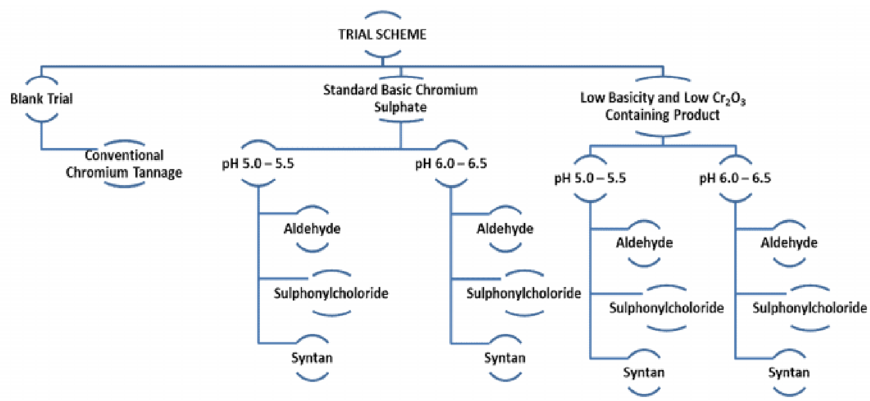

Figure 1. Trial scheme

In residual tanning baths total chromium and COD values were determined according to SM 3120 B and SM 5220 standard methods. After tanning, wet-end processes were carried out in one batch according to company's standard upper leather production route.

Cr_2O_3 contents (ISO 5398-1:2007), shrinkage temperatures (ISO 3380:2015), tensile strengths and percentage extensions (ISO 3376:2011), resistance to grain cracking and grain crack indexes (ISO 3378:2002) and tear loads (ISO 3377-2:2016) of the produced leathers were determined according to related standards.

RESULTS AND DISCUSSION

Cr_2O_3 contents of the leathers and COD values and amount of chromium remaining in residual baths are given in Table 1.

Table 1. Residual bath and leather parameters of tanning trials

pH	Trials	Leather Parameters			Residual Bath	
		Homogeneity	Thickness (mm)	Cr_2O_3 (%)	Cr (mg/L)	COD (mg/L)
-	Blank	Homogen	1.34	3.97	4142	7440
6.0-6.5	LowBasicity&Cr_2O_3 (**LBCr**)	Not Homogen	1.54	3.28	125	4480
6.0-6.5	Cr_ Aldehyde	Not Homogen	1.41	4.65	16.9	11400
6.0-6.5	Cr_ Sulphonylchloryde	Not Homogen	1.55	4.09	64.3	7840
6.0-6.5	Cr_ Syntan-1(F90)	Homogen	1.66	3.18	536	7800
6.0-6.5	**LBCr**_ Aldehyde	Not Homogen	1.46	4.17	88.9	8800
6.0-6.5	**LBCr**_Sulphonylchloryde	Homogen	1.41	4.02	219.2	51200
6.0-6.5	**LBCr**_Syntan-1(F90)	Homogen	1.51	3.38	81.3	4000
5.0-5.5	Cr_ Aldehyde	Not Homogen	1.56	4.37	217.8	760
5.0-5.5	Cr_ Sulphonylchloryde	Not Homogen	1.56	4.83	109.7	3200
5.0-5.5	Cr_ Syntan-1(F90)	Not Homogen	1.51	3.98	661.2	280
5.0-5.5	**LBCr**_Aldehyde	Homogen	1.51	3.96	629	6560
5.0-5.5	**LBCr**_Sulphonylchloryde	Not Homogen	1.43	3.16	340.5	760
5.0-5.5	**LBCr**_Syntan-1(F90)	Homogen	1.65	3.12	1347	8320

Considering the values given in the table it is seen that 4142 mg/L chromium remains in residual bath in conventional chromium tanning system which dramatically decreases to varying values between 16.9 - 1347 mg/L in chromium tanning trials at high initial pH values without pickling. In this new ecological tanning system amount of chromium remaining in residual baths can be reduced up to 67.5 % to 99.5% comparing to conventional tanning while 3.12-4.83% of Cr_2O_3 bound to the leathers depending on the type of system used in trials as presented in Fig.2.

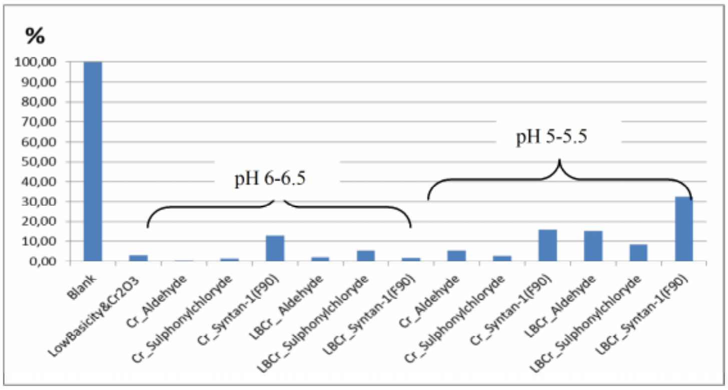

Figure 2. Decrease of chromium remaining in residual bath

From the evaluation and comparison of the physical test results of the leather samples produced higher exhausting technologies with conventional produced leather samples it was seen that most of the physical properties were found comparable with a few exceptions (Table 2).

Table 2. Physical properties of the final leather products

pH	Trials	Leather Parameters					
		Ts (^oC)	Tensile Strength (N/mm^2)	Elonga tion (%)	Lastometer (kg)	Lastometer (mm)	Double Edge Tear (N/mm)
-	Blank	119	18.4	46.1	18.6	7.37	74.18
6.0-6.5	LowBasicity&Cr_2O_3 (**LBCr**)	112	20.1	60.1	16.4	6.65	113.85
6.0-6.5	Cr_Aldehyde	118	12.9	40.8	19.7	7.42	65.21
6.0-6.5	Cr_Sulphonylchloryde	120	16.7	63.9	15.0	6.51	105.70
6.0-6.5	Cr_Syntan-1(F90)	115	14.4	46.0	21.9	7.61	91.43
6.0-6.5	**LBCr**_ Aldehyde	115	17.7	59.2	20.4	6.68	95.40
6.0-6.5	**LBCr**_Sulphonylchloryde	119	15.2	53.2	20.2	7.94	79.99
6.0-6.5	**LBCr**_Syntan-1(F90)	119	17.4	50.5	21.5	7.27	108.56
5.0-5.5	Cr_Aldehyde	119	10.1	46.6	15.8	7.10	70.45
5.0-5.5	Cr_Sulphonylchloryde	115	17.6	56.3	25.8	9.08	111.15
5.0-5.5	Cr_Syntan-1(F90)	121	16.2	56.2	20.8	7.10	113.55
5.0-5.5	**LBCr**_Aldehyde	118	15.4	57.9	21.4	7.54	80.72
5.0-5.5	**LBCr**_Sulphonylchloryde	119	12.7	68.7	25.8	8.37	64.92
5.0-5.5	**LBCr**_Syntan-1(F90)	119	13.5	61.1	23.1	7.52	84.77

Besides consideration and evaluation of chemical and physical data obtained from the analysis and tests, a committee comprising members from production supervisors, quality control and marketing departments of the company, made evaluations considering their existing product properties in terms of handle, touch and physical appearance and costumer demands. From the final evaluations considering both physical and chemical data and committee's remarks it was concluded that best results were obtained from Cr_Aldehyde, Cr_Sulphonylchloryde, Cr_Syntan-1(F90), LBCr_Syntan-1(F90) trials conducted at pH 5-5.5 and decided to make further studies to improve and verify these process designs in higher batches.

CONCLUSIONS

The approach handled in this research for ecological chromium tanning without pickling process and offering less chromium salts at higher initial pH values has been successfully applied in to the practice in pilot scale and chromium remaining in residual baths could be reduced up to 99.5% by alternative formulations comparing with conventional tanning.

Along with decreasing the amount of residual chromium, this approach has also the benefits of considerable decrease in load of treatment plant associated with noticeable decreases in chromium and salt in effluents, reducing treatment costs and potential utilization of sludge i.e. as compost.

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REFERENCES

Luan, S., Liu, Y. and Fan, H. (2007), "A novel pretanning agent for high exhaustion chromium tannage", *Journal of the Society of Leather Technologists and Chemists*, 91(4): 149-151.

Luo, Z., Zhang, X., Fan, H. *et al*. (2009), "Modification of collagen for high Cr(III) absorption", *Journal of the American Leather Chemists Association*, 104(4), 152-161.

Morera, J.M., Bacardit, A., Olle, L., Costa, J. and Germann, H.P. (2006), "Study of a Chrome Tanning Process without Float and With Low-Salt Content As Compared to A Traditional Process, Part II", *Journal of the American Leather Chemists Association*, 101(12), 454-460.

Research and Development Department, Seta S/A, Brazil (2000), "Rationalization of the tanning process: avoiding pickling and basification", *World Leather*, October, 67-71.

Sreeram, K.J., Raghava Rao, J., Chandrababu, N.K., Nair, B.U. and Ramasami, T. (2006), "High Exhaust Chrome-Aluminium Combination Tanning: Part 1. Optimization of Tanning", *Journal of the American Leather Chemists Association*, 101(3), 86-95.

Sundar, V.J., Rangasamy, T., Sivakumar, V. and Muralidharan, C. (2007), "A Novel Pickle-Free High Exhaust Chrome Tanning Method-An Approach for Total Dissolved Solids Management", *Journal of the Society of Leather Technologists and Chemists*, 88(5), 252-255.

Tao, E., Hong-Rui, M. and Hao, C. (2014), "The Quantitative Calculation Between Chrome Technological Parameters in Leather Making and Chrome Absorptivity" *Journal of the Society of Leather Technologists and Chemists*, 98, 63-68.

Thanikaivelan, P., Kanthimathi, M., Raghava Rao, J. and Unni Nair, B. (2002), "A Novel Formaldehyde-Free Synthetic Chrome Tanning Agent For Pickle-Less Chrome Tanning: Comparative Study On Syntan Versus Modified Basic Chromium Sulfate", *Journal of the American Leather Chemists Association*, 97(4), 127-136.

*** ISO 3376:2011 Determination of tensile strength and percentage extension

*** ISO 3377-2:2002 Determination of tear load -- Part 2: Double edge tear

*** ISO 3378:2002 Determination of resistance to grain cracking and grain crack index

*** ISO 3380:2015 Determination of shrinkage temperature

*** ISO 5398-1:2007 Chemical determination of chromic oxide content -- Part 1: Quantification by titration

*** SM 3120 B:2005, Standard Methods for Examinations of Water and Wastewater. Metals by plasma emission spectrometry, American Water Works Association, 2005.

*** SM 5220 B: Chemical Oxygen Demand (COD), Opened Reflux- Closed Reflux, Titrimetric Method.