PILOT SCALE TRIALS FOR HIGHER EXHAUSTING CHROMIUM TANNING

HASAN ÖZGÜNEY¹, MEHMET METE MUTLU¹, CEMILE CEREN TOSUN², ÖZGÜR DEMİRCİ², ONUR ABALI², YIGIT KAMAN², TALIP SEPİCİ²

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

²Sepiciler Caybasi Leather Company, Mustafa Kemal Atatürk Mah. İzmir - Aydın Asfaltı Cad.
No: 110 Torbalı - İzmir 35860, Türkiye, Phone: +90 232 850 50 00

Chromium tanning is a matter of high concern due to chromium containing effluents and wastes. More ecologic systems with less chromium usage or chrome-free production systems are subject of studies in recent years. One of the approaches in this concern is to use non-pickling systems and higher initial pH to increase exhaustion in chromium tanning. However adopting this system in leather industry has some challenges like to assure the same quality. In a project with one of the leading companies in Turkish Leather Industry, higher exhausting chromium tanning system has been planned to be tried in laboratory, pilot and industrial scales respectively with various pH and pre-tanning agent parameter changes. In the present stage (pilot scale trials) of the project, best resulting formulations from the laboratory scale trials were carried out to pilot scale (500kg batches) by expanding the trials with additional pre-tanning agents. From the results, it was seen that chromium remaining in the baths were varying between 325 - 875 mg/L. Which means amount of chromium remaining in residual baths could be reduced up to 78.87 % to 92.15% comparing to conventional tanning while 2.9-4.7% of Cr₂O₃ bound to the leathers depending on the type of system used in pilot scale trials.

Keywords: Leather, Chromium Tannage, High Exhaustion

INTRODUCTION

Due to the excellent properties of chrome as a tanning agent, a majority of leathers are produced by chrome tanning method (Sundar *et al.*, 2002) but 90% of chrome tanned leathers shows only a 60-70% uptake of chrome (Cui, 2017).

Chromium tanning is followed closely due to chromium containing effluents and wastes. More ecologic systems with less chromium usage or chrome-free production systems are subject of studies in recent years. One of the approaches in this concern is to use non-pickling systems and higher initial pH to increase exhaustion in chromium tanning. However adopting this system in leather industry has some challenges like to assure the same quality.

Kumar *et al.* (2011) have evaluated chrome tanning process for its “greenness” by using a prominent tool named atom economy (the conversion efficiency of a chemical process in terms of all atoms involved) for four types of chrome tanning processes: direct chrome liquor recycle, ethanol-amine assisted, pickleless chrome tanning and conventional chrome tanning. Among the four improved methods of chrome tanning evaluated, the pickles chrome tanning method provided the maximum atom economy.

In this project namely “Environmentally Friendly Chromium Tanning Technology” the higher exhausting chromium tanning system has been tried to be adopted with one of the leading companies in Turkish Leather Industry in three stages: 1-Laboratory trials at the stage of transition from concept to design, 2-Pilot scale trials at the stage of design development and verification works and 3-Industrial scale trials at the stage of experimental production and reporting. In first stage, laboratory based trials (50kg batches) were done with 3 pre-tanning agents, 2 chromium tanning agents and 2

different pHs. The results of the first stage was given in ICAMS 2016 (Ozgunay *et al.*, 2016). In second stage of the project, best resulting formulations from laboratory scale trials were carried out to pilot scale (500kg batches) by expanding the trials with additional pre-tanning agents. In this paper the results of stage 2: pilot scale trials will be discussed.

MATERIAL AND METHOD

Lime split domestic pelts (to be approx. 500 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.

From the evaluations of stage 1 (laboratory scale); considering both physical and chemical data and committee's remarks it was concluded that best results were obtained from Cr_Aldehyde, Cr_Sulphonylchloride, Cr_Synton-1(F90), LBCr_Synton-1(F90) trials conducted at pH 5-5.5 (Ozgunay *et al.*, 2016). It was decided to make further studies to improve and verify these process designs in higher batches at pH 5.5-6.0. Additionally the committee offered to include 2 more synthetic tannins ((Synton-2(HS) and Synton-3(CAT)) to the trials considering the promising results of Synton-1(F90). So an aldehyde, a sulphonylchloride and 3 syntans 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 5.5-6.0 and chromium tanning was performed by using 5% standard basic chromium sulphate and 6% of a commercial chromium tanning agent having lower basicity and Cr₂O₃. The trial scheme is given in Fig.1.

In residual tanning baths total chromium and COD values were determined according to SM 3120 B (2005) and SM 5220 (2005) standard methods. Cr₂O₃ contents (ISO 5398-1:2007), shrinkage temperatures (ISO 3380:2015), tensile strengths and percentage extensions (ISO 3376:2011), and tear loads (ISO 3377-2:2016.) of the produced leathers were determined according to related standards.

Figure 1. Pilot Scale Trial Scheme

RESULTS AND DISCUSSION

In Table 1 & Table 2, parameters of residual baths and properties of obtained leathers belonging to trials are given. When Table 1 is investigated, it is seen that chromium in the remaining baths were varying between 325 - 875 mg/L (Table 1). Which means amount of chromium remaining in residual baths could be reduced up to 78.87 % to 92.15% comparing to conventional tanning while 2.9-4.7% of Cr_2O_3 bound to the leathers depending on the type of system used in pilot scale trials as presented in Fig.2. Accordingly, with the increased consumption, COD values of residual baths decreased noticeably comparing with conventional chromium tanning system. Furthermore, regarding homogeneity parameter, the distribution of chromium through cross-section was found homogen for all samples by increasing mechanical effect and by the pH shift. Thus, homogeneity problem, which was a bothering issue in laboratory scale trials was, overcome (Ozgunay *et al.*, 2016).

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	1.25	4.07	4142	15000
5.5-6.0	Cr_ Aldehyde	Homogen	1.65	4.50	325	4800
5.5-6.0	Cr_ Sulphonylchloride	Homogen	1.61	4.70	383	5200
5.5-6.0	Cr_ Syntan-1(F90)	Homogen	1.62	4.10	520	6880
5.5-6.0	Cr_ Syntan-2(HS)	Homogen	1.53	3.40	875	11500
5.5-6.0	Cr_ Syntan-3(CAT)	Homogen	1.57	4.10	400	8400
5.5-6.0	LBCr_ Syntan-1(F90)	Homogen	1.53	2.90	405	8006

Figure 2. Comparison of mg/L chromium in residual baths of pilot scale trials

From the evaluation and comparison of the physical test results of the pilot scale trials' leather samples with conventional produced leather samples it was seen that most of the physical properties were found better or comparable but a few exceptions in shrinkage temperature (Table 2). Considering shrinkage temperatures of trials, only Cr_Syntan-3(CAT) sample gave noticeable lower shrinkage temperature (101°C) than the Blank. However, the increment in Double Edge Tear values of this higher exhaustion system was remarkable.

Table 2. Physical properties of the final leather products of pilot scale trials

pH	Trials	Leather Parameters			
		Ts (°C)	Tensile Strength (N/mm ²)	Elongation (%)	Double Edge Tear (N/mm)
-	Blank	110	11.9	51.6	46.0
5.5-6.0	Cr_Aldehyde	124	13.9	50.3	108.4
5.5-6.0	Cr_Sulphonylchoryde	118	15.2	45.8	95.9
5.5-6.0	Cr_Syntan-1(F90)	121	18.4	50.2	111.5
5.5-6.0	Cr_Syntan-2(HS)	108	12.3	45.2	77.3
5.5-6.0	Cr_Syntan-3(CAT)	101	15.5	45.3	100.0
5.5-6.0	LBCr_Syntan-1(F90)	109	20.5	50.9	119.4

CONCLUSION

In leather production, scaling up the laboratory trials to industrial scale may be problematic due to varying process conditions and the results may vary extremely. For this reason pilot scale trials at the stage of design development and verification works are necessary. In the present of the project, the trials giving the best results in laboratory scale were verified and improved

From the results, it was seen that chromium remaining baths were varying between 325 - 875 mg/L, which means amount of chromium remaining in residual baths could be reduced up to 78.87 % to 92.15% comparing to conventional tanning system. Accordingly, COD values of residual baths were also decreased noticeably.

The homogeneity problem, which was a bothering issue in laboratory scale trials was, overcome in pilot scale trials.

From the evaluation and comparison of the physical test results of the pilot scale trials' leather samples with conventional produced leather samples it was seen that most of the physical properties were found better or comparable

The results of pilot scale trials of this higher exhausting chromium tanning system were found to be promising to be used in industrial scale trials at the stage of experimental production.

Acknowledgements

This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under Grant [Project number 3140017].

REFERENCES

- American Water Works Association (2005), Standard Methods for Examinations of Water and Wastewater. Metals by plasma emission spectrometry, SM 3120 B:2005.
- American Water Works Association (2005), Chemical Oxygen Demand (COD), Opened Reflux-Closed Reflux, Titrimetric Method, SM 5220 B:2005.
- Cui, L. *et al.* (2017), "A Cleaner Method for Low-Chrome Tanning with No-Salt Pickling", *JSLTC*, 101, 219-226.
- International Organization for Standardization (2007), Chemical determination of chromic oxide content -- Part 1: Quantification by titration, ISO 5398-1:2007.
- International Organization for Standardization (2015), Determination of shrinkage temperature, ISO 3380:2015.
- International Organization for Standardization (2011), Determination of tensile strength and percentage extension, ISO 3376:2011.
- International Organization for Standardization (2016), Determination of tear load -- Part 2: Double edge tear, 3377-2:2016.
- Pradeep Kumar, M. *et al.* (2011), "Green Chemistry Approach in Leather Processing: A Case of Chrome Tanning", *JALCA*, 106, 113-120.
- Ozgunay, H. *et al.* (2016), "Industrial Trials For a More Ecological Chromium Tanning", *Proceedings of the 6th International Conference on Advanced Materials and Systems*, ICAMS 2016, Bucharest-Romania, <https://doi.org/10.24264/icams-2016.IV.9>.
- Sundar, V.J. *et al.* (2002), "Cleaner Chrome Tanning Emerging Options.", *J. Clean. Prod.*, 10, 69, [https://doi.org/10.1016/S0959-6526\(01\)00015-4](https://doi.org/10.1016/S0959-6526(01)00015-4).