PRACTICES ON ECOLOGICAL CHROMIUM TANNING SYSTEM

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ABSTRACT. Chromium tanning using less chromium salts at higher initial pH values is one of the approaches offered in recent years in order to overcome environmental problems caused by conventional chromium tanning. However this system couldn't be directly switched to application due to its potential risks. In the present study this ecological approach was investigated at industrial scale. The variables used in the research were: pre-tanning agents, initial pH of tanning and tanning agents. Various wet-end and finishing processes depending on three different types of products were applied according to the company's production line. Chromium contents of the leathers and remaining amounts in effluents were determined for each trial. Also, the physical properties of the leathers were investigated. Along with maintaining similar properties and quality from the produced leathers, chromium remaining in residual baths could be reduced up to 92 and 76% by alternative formulations respectively in 500 kg and 6000 kg batches.
KEY WORDS: leather, chromium tannage, high exhaustion

PRACTICI PRIVIND SISTEMUL DE TĂBĂCIRE ECOLOGICĂ ÎN CROM

REZUMAT. Tăbăcirea în crom care utilizează mai puţine săruri de crom la valori iniţiale mai ridicate ale pH-ului este una din abordările apărute în ultimii ani pentru a rezolva problemele de mediu cauzate de tăbăcirea convenţională în crom. Cu toate acestea, acest sistem nu a putut fi pus în aplicare în mod direct din cauza potenţialelor riscuri. În studiul de faţă această abordare ecologică a fost investigată la scară industrială. Variabilele utilizate în cercetare au fost: agenţi de pre-tăbăcire, pH iniţial al tăbăcirii şi agenţilor de tăbăcire. Au fost aplicate diferite procedee umede şi finisaje în funcţie de trei tipuri diferite de produse, conform liniei de producţie a companiei. Conţinutul de crom din piele şi cantităţile rămase în efluenţi au fost determinate pentru fiecare încercare. De asemenea, au fost investigate proprietăţile fizice ale pielii. Pe lângă menţinerea unor proprietăţi şi a calităţii pielii fabricate, cromul rămas în flotele reziduale ar putea fi redus până la 92 şi 76% prin recepturi alternative, în loturi de 500 kg, respectiv de 6000 kg.
CUVINTE CHEIE: piele, tăbăcire în crom, epuizare mare

PRATIQUES SUR LE SYSTÈME DE TANNAGE ÉCOLOGIQUE AU CHROME

RÉSUMÉ. Le tannage au chrome utilisant moins de sels de chrome à des pH initiaux plus élevés, est l'une des approches proposées ces dernières années pour surmonter les problèmes environnementaux causés par le tannage au chrome conventionnel. Cependant, ce système ne pouvait pas être directement transféré à l'application en raison de ses risques potentiels. Dans la présente étude, cette approche écologique a été étudiée à l'échelle industrielle. Les variables utilisées dans la recherche étaient: agents de prétannage, pH initial du tannage et des agents de tannage. Différents procédés par voie humide et de finition ont été appliqués avec trois types de produits différents, en fonction de la chaîne de production de l'entreprise. Les teneurs en chrome des cuirs et les quantités restantes dans les effluents ont été déterminées pour chaque essai. De plus, les propriétés physiques des cuirs ont été étudiées. En plus de maintenir les propriétés et une qualité similaires des cuirs produits, le chrome restant dans les bains résiduels pourrait être réduit jusqu'à 92 et 76% par des formulations alternatives en lots de 500 kg et respectivement 6 000 kg.
MOTS CLÉS : cuir, tannage au chrome, épuisement de bain élevé

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INTRODUCTION

As the hides/skins are protein based, they are putrescible by bacterial activity in wet-form until tanning process. The tanning process is the stabilization of the collagen matrix to retain a separated fiber structure and to increase the hydrothermal stability. This is the stage at which the pelt becomes "leather" and is then resistant to putrefaction or rotting. Organic or inorganic based materials which are able to crosslink with reactive groups of the collagen are used in the tanning process [1].

Modern tanning chemistry can be classified by mineral tanning, vegetable tanning, oil tanning, aldehyde tanning, syntans, and organic tanning. Chrome, among mineral tanning materials is the most widely used tanning material in leather production due to its unique features that it gives to the leather. Chrome tanning provides better leather characteristics than other tanning materials such as high thermal stability, light weight and high strength properties [2].

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 [3-5]. So, the conventional chrome tanning method is associated with large release of chromium content in the effluent [6].

Although the methods of recycling chrome are well known and applied, pollution related to chrome continues to be one of the most important problems in leather industry [7, 8].

Chromium compounds are among dangerous wastes, and they have several harmful impacts on soil, water and living beings due to their toxic effects. For example, Cr(III) content between 10-100 ppm in soil affects the microorganism population and reduces CO_2 formation, therefore it affects the biological reactions in soil in the negative way. Wastewaters that include chrome reduce the efficiency of the soil when discharged to agricultural land, and prevent the growth of the plants in these lands [9].

Treatment, storage and disposal of this chromium containing effluents and sludge pose 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 [10-14]. Among these alternatives, higher exhausting chromium tanning technology applied at higher initial pH values without pickling by lower chromium offer has been 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 laboratory, pilot and industrial scales 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.

EXPERIMENTAL

Materials and Methods

Lime split domestic (bovine hides from Ankara region) 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 for each pH value chromium tanning was performed independently 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.

In residual tanning baths total chromium and COD values were determined according to SM 3120 B and SM 5220 standard methods [15, 16]. After tanning, wet-end processes were carried out in one batch according to company's standard upper leather production route.

Cr_2O_3 contents [17], shrinkage temperatures [18], tensile strengths and percentage extensions [19], resistance to grain cracking and grain crack indexes [20] and tear loads [21] of the produced leathers were determined according to related standards.

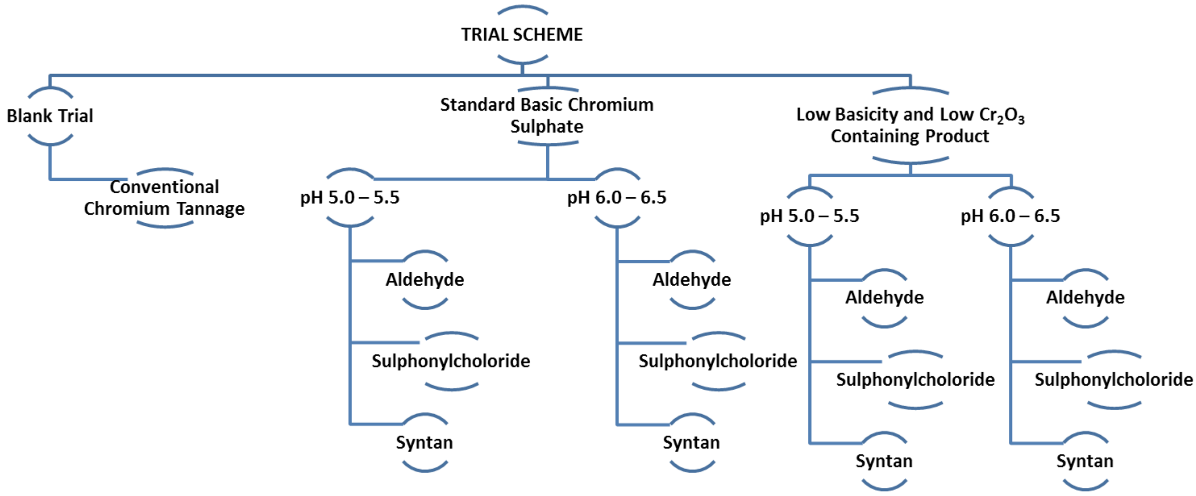

Figure 1. Trial scheme

RESULTS AND DISCUSSIONS

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

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.

The key to this system lies in the reaction with the collagen polypeptide chain. By introducing additional anionic groups, the iso-electric point (IEP) is effectively shifted from conventional IEP of collagen. This shift in IEP of the polypeptide chain enables faster chromium penetration during tannage at pH 4.5-6.0 than conventional tanning at a pH of 3.0. The chrome fixation is also improved due to the increased number of non-ionised carboxyl groups in collagen [3].

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 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)
-	Conventional Cr tanning	Homogenous	1.34	3.97	4142	7440
6.0-6.5	LowBasicity&Cr_2O_3 (LBCr)	Not Homogenous	1.54	3.28	125	4480
6.0-6.5	Cr_ Aldehyde	Not Homogenous	1.41	4.65	16.9	11400
6.0-6.5	Cr_ Sulphonylchloryde	Not Homogenous	1.55	4.09	64.3	7840
6.0-6.5	Cr_ Syntan-1(F90)	Homogenous	1.66	3.18	536	7800
6.0-6.5	LBCr_ Aldehyde	Not Homogenous	1.46	4.17	88.9	8800
6.0-6.5	LBCr_Sulphonylchloryde	Homogenous	1.41	4.02	219.2	51200
6.0-6.5	LBCr_Syntan-1(F90)	Homogenous	1.51	3.38	81.3	4000
5.0-5.5	Cr_ Aldehyde	Not Homogenous	1.56	4.37	217.8	760
5.0-5.5	Cr_ Sulphonylchloryde	Not Homogenous	1.56	4.83	109.7	3200
5.0-5.5	Cr_ Syntan-1(F90)	Not Homogenous	1.51	3.98	661.2	280
5.0-5.5	LBCr_Aldehyde	Homogenous	1.51	3.96	629	6560
5.0-5.5	LBCr_Sulphonylchloryde	Not Homogenous	1.43	3.16	340.5	760
5.0-5.5	LBCr_Syntan-1(F90)	Homogenous	1.65	3.12	1347	8320

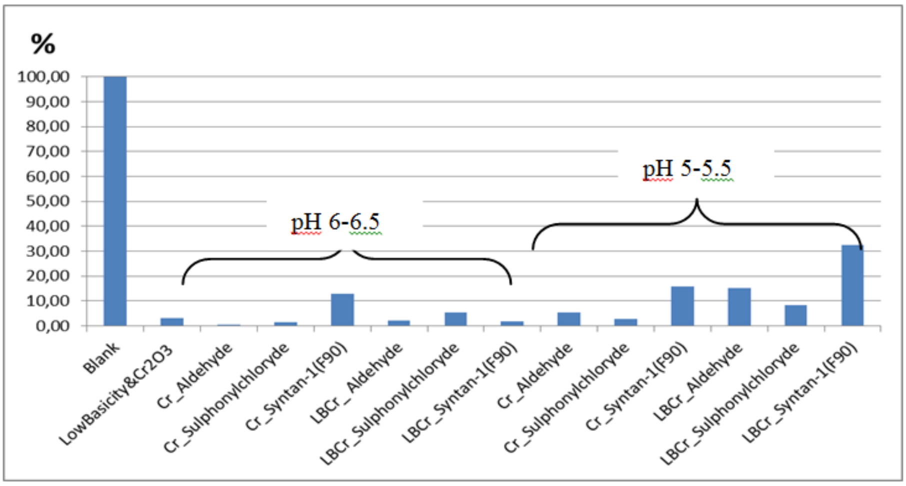

Figure 2. Comparison of mg/L chromium in residual baths

Table 2: Physical properties of the final leather products

pH	Trials	Leather Parameters					
		Ts (°C)	Tensile Strength (N/mm^2)	Elongation (%)	Lastometer (kg)	Lastometer mm	Double Edge Tear (N/mm)
-	Conventional Cr tanning	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 at pH 5.5-6.0. Additionally the committee offered to include two more synthetic tannins ((Syntan-2(HS) and Syntan-3(CAT)) to the trials considering the promising results of Syntan-1(F90).

The verification trials were conducted with 500kg of batches of pelts to simulate industrial scale production.

Table 3. Residual bath and leather parameters of verification trials

pH	Trials	Leather Parameters			Residual Bath	
		Homogeneity	Thickness (mm)	Cr_2O_3 (%)	Cr (mg/L)	COD (mg/L)
-	Conventional Cr tanning	Homogenous	1.25	4.07	4142	15000
5.5-6.0	Cr_ Aldehyde	Homogenous	1.65	4.50	325	4800
5.5-6.0	Cr_ Sulphonylchloryde	Homogenous	1.61	4.70	383	5200
5.5-6.0	Cr_ Syntan-1(F90)	Homogenous	1.62	4.10	520	6880
5.5-6.0	Cr_ Syntan-2(HS)	Homogenous	1.53	3.40	875	11500
5.5-6.0	Cr_ Syntan-3(CAT)	Homogenous	1.57	4.10	400	8400
5.5-6.0	LBCr_Syntan-1(F90)	Homogenous	1.53	2.90	405	8006

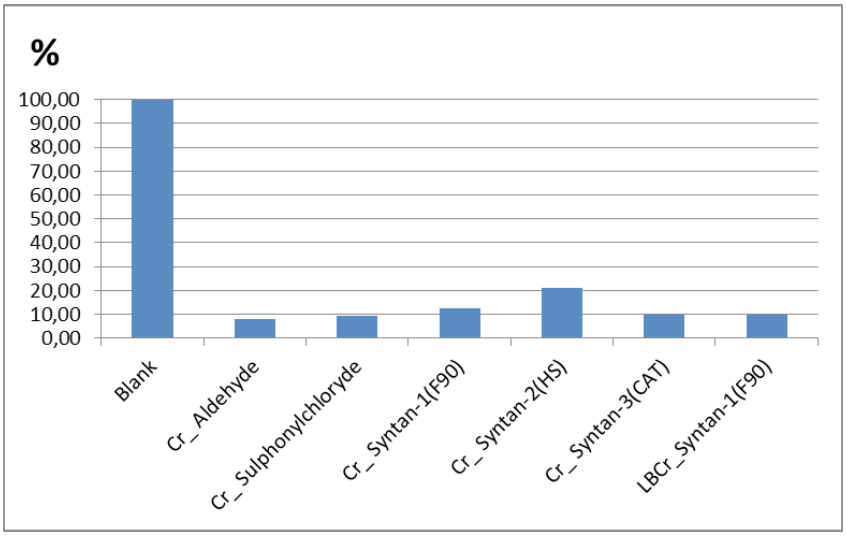

Figure 3. Comparison of mg/L chromium in residual baths of verification trials

In verification trials it was seen that chromium remaining baths were varying between 325-875 mg/L (Table 3), which means the 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 verification trials as presented in Fig. 3.

Table 4: Physical properties of the final leather products of verification trials

pH	Trials	Leather Parameters			
		Ts (°C)	Tensile Strength (N/mm²)	Elongation (%)	Double Edge Tear (N/mm)
-	Conventional Cr tanning	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_Sulphonylchloryde	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

From the evaluation and comparison of the physical test results of the verification 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 4).

Besides consideration and evaluation of chemical and physical data obtained from the analysis and tests, the evaluation committee of the company, re-made evaluations and concluded to make industrial scale (6 tons of hide) trials with Cr_ Syntan-1(F90) and Cr_ Syntan-2(HS).

Table 5: Residual bath and leather parameters of industrial trials

pH	Trials	Leather Parameters			Residual Bath	
		Homogeneity	Thickness (mm)	Cr_2O_3 (%)	Cr (mg/L)	COD (mg/L)
5.5-6.0	Cr_ Syntan-1(F90)	Homogenous	1.01	4.65	1750	7400
5.5-6.0	Cr_ Syntan-2(HS)	Homogenous	1.11	3.60	1000	8500

In industrial trials chromium remaining baths were found to be 1750 and 1000 mg/L (Table 5) for Cr_ Syntan-1(F90) and Cr_ Syntan-2(HS) respectively. Which means amount of chromium remaining in residual baths could be reduced 57.75 and 75.86% comparing to conventional tanning and 4.65 and 3.60% of Cr_2O_3 were bound to the leathers.

Table 6: Physical properties of the final leather products of industrial trials

pH	Trials	Leather Parameters			
		Ts (°C)	Tensile Strength (N/mm²)	Elongation (%)	Double Edge Tear (N/mm)
5.5-6.0	Cr_ Syntan-1(F90)	110	10.3	37.6	38.2
5.5-6.0	Cr_ Syntan-2(HS)	103	9.6	30.1	27.8

The physical test results of the verification trials' leather samples are given in Table 6. Although some of the physical test results of the leathers seem to be slightly lower comparing with conventional produced leather samples, taking in consideration the product type chosen to be produced, organoleptic controls and fulfillment of customer desires, the committee concluded that the results were satisfactory.

CONCLUSIONS

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 the present project one of these approaches: chromium tanning without pickling process, using less chromium salts at higher initial pH is tried in industrial scale at a leading company in Turkish leather industry.

The theory was applied at laboratory, pilot and finally industrial scale with various tanning parameters like different initial pH values and pre-tanning materials. 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 amount of chromium remaining in residual baths could be reduced up to 99.5%, 92.15% and 75.86% in laboratory, pilot and industrial scale productions, respectively comparing to conventional tanning with satisfactory chromium contents and leather properties.

Along with decreasing the amount of residual chromium, this approach also offers 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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