

MONITORING AND OPTIMISATION OF CHROMIUM UPTAKE IN TANNING PROCESS IN LEATHER MANUFACTURE BY USING SPECTROPHOTOMETRY

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Abstract

In the present study leather samples have been tanned with various application times of temperature and basification; and chromium exhaustion of the process has been monitored by measuring the chromium concentration of the float with a spectrophotometer in short time intervals (5 -10 minutes). Optimal conditions of chromium tannage have been tried to be determined by comparing the data obtained from graphics and results of the physical tests and chemical analysis applied to the leather samples. Consequently, online monitoring of chromium process by using spectrophotometric measurements can be used in chromium tanning process in leather manufacturing for efficient process control and optimization.

Key words: leather, chromium tannage, spectrophotometry

1. INTRODUCTION

Tanning is a process of converting unstable raw hides into leather, with adequate strength properties and resistance to various biological and physical agents. In many languages distinction is made between leather and hides or skins, others have a common term for all of them (Bienkiewicz 1983).

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 fibre 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. The reactive group used in fixation/binding differs depending on the type of the tanning material. For example; while mineral tanning materials (chromium, aluminium, and zirconium) react with carboxyl groups of the collagen; vegetable tannins, aldehydes, and syntans react with amino groups. These reactions change the number of the reactive groups available, and charge balance of the collagen for further processes and chemicals (Ozgunay et al. 2009).

Chromium tannage is the most widely used tannage system in leather manufacturing due to its unique properties like softness, high hydrothermal stability, simple application technique and being suitable for versatile leather types. However, in a conventional chromium tanning process, 1/3 to 1/4 of the used chromium remains in residual baths. Since chromium is a heavy metal, chromium discharge poses a major problem and is being discussed seriously. Optimizing the chromium tanning process and increasing chromium exhaustion is a popular topic of research in recent years.

When we talk about tanning today, the topic is usually raised in connection with environmental compatibility. Due to the increasingly stringent requirements governing tannery effluents as regards their chrome content, and due to a variety of problems involved in the disposal or utilization of by-products containing chrome, chrome tannage in particular has recently come under criticism (Germann 1995).

Usually companies take samples and check the chromium content of leathers and waste water at the end of chromium tanning process. Chromium contents are generally controlled by chemical determination of chromic oxide content via quantification by titration. This method is applied in a laboratory and takes several hours to get results. This gives a data of what already realized but it is not possible to direct the process in real time.

Determining concentration of a coloured liquid using Lambert-beer law is a fast and popular technique in instrumental analysis applications. The results can be obtained in seconds after a proper calibration

curve is prepared and no chemical operations are needed. Borrás et al. (1999), have obtained 1.9% accuracy for the chromium determination for a study in simultaneous determination of chromium and basicity in tanning liquors using spectrophotometry and multivariate calibration.

In the present study leather samples have been tanned with various application times of temperature and basification; and chromium exhaustion of the process has been monitored by measuring the chromium concentration of the float with a spectrophotometer in short time intervals (5 -10 minutes). Optimal conditions of chromium tannage have been tried to be determined by comparing the data obtained from graphics and results of the physical tests and chemical analysis applied to the leather samples.

2. MATERIAL AND METHODS

2.1. Materials

15 pickled New Zealand originated sheep skins were used as material for tanning trials. A double beam Shimadzu 1601 spectrophotometer and 1x1x4 cm Helma quartz cuvettes were used for spectrophotometric measurements.

Technical grade acids and alkalis, and commercial chromium sulphate with 25.5% Cr₂O₃ content, 33% Schorlemmer basicity were used in process recipes.

2.2. Leather processing methods

Pickled sheep skins were taken into depickling process. After bating, degreasing and washing processes; the pelts were adjusted to pH 2.8 with pickling process. Then the leather samples were tanned according to the chromium tanning recipe given in Table 1, by using temperature and basification time parameter variations given in Table 2.

Table 1. Standard chromium tanning recipe

Process	Product	Dosage (%)	Temperature (°C)	Duration	Remarks
Chromium Tanning	Water	100	25		
	Salt	10			
	HCOOH	0.5		10 min.	
	Commercial Chromium Powder	10	*	6 h	
	HCOONa	2.5		*	pH=4.0

* Temperature and basification time variations are given in Table 2

Table 2. Temperature and basification variations for chromium tanning trials

BLANK		No heating	
Process	Application Time	%	Substance
Chromium Tanning	5 hours		
Basification	1 hour	1.25	HCOONa
		1.25	HCOONa
EARLY HEATING TANNING (A1)		40°C for 6 hours	
Process	Application Time	%	Substance
Early Basification (B1)	30 minutes later	1.25	HCOONa
	60 minutes later	1.25	HCOONa
Mid Basification (B2)	2 hours 30 minutes later	1.25	HCOONa
	3 hours later	1.25	HCOONa
Continuous Basification (B3)	Every 60 minutes after first 30 minutes	0.4	HCOONa
HEATING IN MIDDLE OF TANNING (A2)		20°C for first 3 hours 40°C for last 3 hours	
Process	Application Time	%	Substance
Early Basification (B1)	30 minutes later	1.25	HCOONa
	60 minutes later	1.25	HCOONa
Mid Basification (B2)	2 hours 30 minutes later	1.25	HCOONa
	3 hours later	1.25	HCOONa
Continuous Basification (B3)	Every 60 minutes after first 30 minutes	0.4	HCOONa
HEATING AT THE END OF TANNING (A3)		20°C for for 4 hours 45 minutes 40°C for last 1 hours 15 minutes	
Process	Application Time	%	Substance
Early Basification (B1)	30 minutes later	1.25	HCOONa
	60 minutes later	1.25	HCOONa
Mid Basification (B2)	2 hours 30 minutes later	1.25	HCOONa
	3 hours later	1.25	HCOONa
Continuous Basification (B3)	Every 60 minutes after first 30 minutes	0.4	HCOONa

Sharphouse (1989), states under the title of warm float that after the chrome salt has penetrated the interior of the skin (as shown by cutting the skin and observing a uniform blue-green cross section) a float of hot water (60-70°C) addition raises the temperature to about 40°C and in the presence of hot water the chrome salts hydrolyse to a greater extend, thereby producing a more basic chrome salt of higher astringency.

After tanning, wet-end processes were carried out in one batch according to a standard garment production route.

2.3. Spectrophotometric Method

At first, absorbance spectrum of a standard chromium solution was plot between 400-800nm Fig.1. Maximum absorption peaks were found to be at 428 nm and 593 nm typical for Chromium III. 428 nm was selected for spectrophotometric measurements. Later, absorptions of known concentrations of 0.25 %, 1.25% and 2.5% chromium solutions were measured at 428nm and a calibration curve was calculated. Finally during tanning water samples were taken from the process bath in every 5 minutes for the first hour and in every 10 minutes for the following 5 hours. Chromium contents of samples were calculated by using the spectrophotometer software based on the calibration curve. The chromium concentrations during the chromium tanning process were plotted versus time.

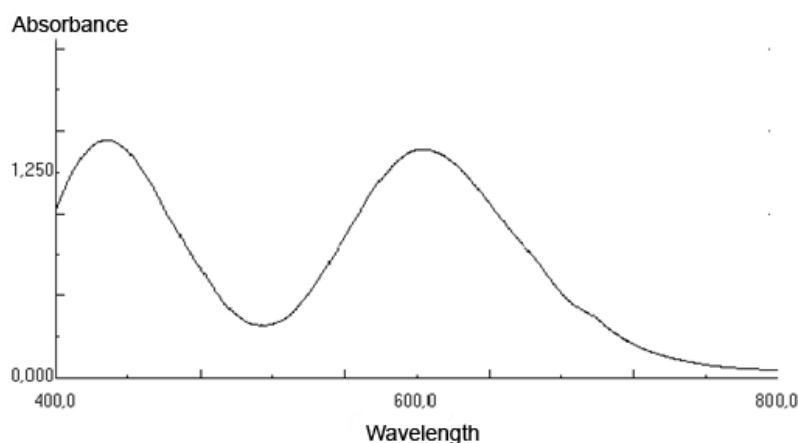


Fig. 1. Absorption spectrum of chromium III solution

Marjoniemi (1995) has also worked determination of Chromium concentration by spectroscopy and modelling. The chromium concentration range of the calibration and test samples used was 0.2 to 7.2 g/l. The lowest prediction error of chromium content was obtained using artificial neural networks with a standard error of 0.197 g/l.

2.4. Test and Analysis Methods

The leather samples were sampled and prepared for chemical analysis and physical tests according to related standards: SLC 1, SLC 2 and SLP 3 (SLTC 1996). Shrinkage temperatures of leathers were measured using the SLP 18 - Measurement of Shrinkage Temperature standard (SLTC 1996). The chromium oxide contents of processed leathers were analysed according to SLC 8 - Determination of Chromic Oxide standard (SLTC 1996). Tensile strengths and percentage extensions and tear loads of the finished leathers were determined according to related standards: SLP 6 and SLP 7 (SLTC 1996).

3. RESULTS AND DISCUSSION

The change of $\text{Cr}_2\text{O}_3\%$ in process baths depending on temperature and basification time changes during chromium tanning process monitored with 5-10 minutes intervals are given in Figure 2. It is seen that chromium uptake by the leather takes place quickly in the first 30-60 minutes of chromium tanning process. So it is important for uniform chromium uptake and distribution that the process drum should not stop at in the first 30-60 minutes. The graphics also show that chromium exhaustion increases by heat and basification applications. Cr_2O_3 contents of process baths are given in Figure 2.

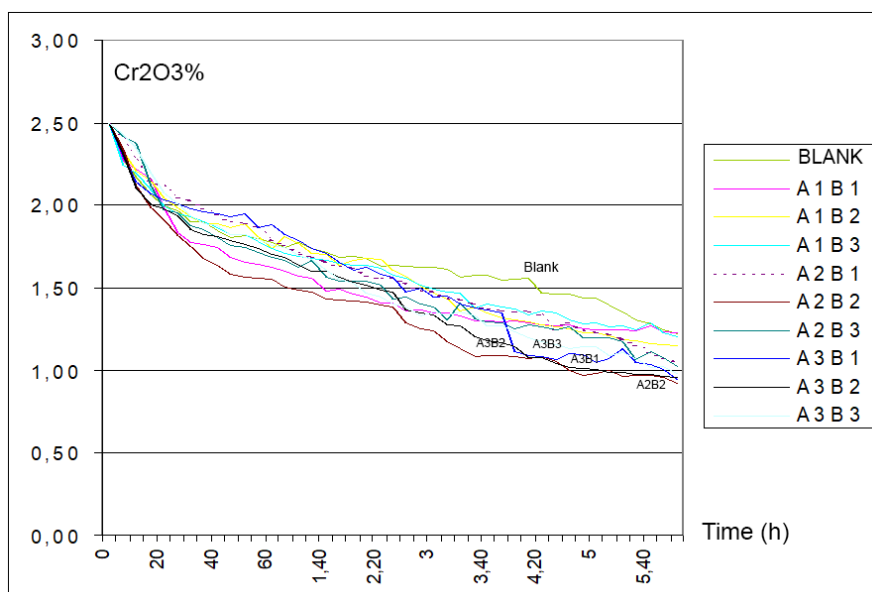
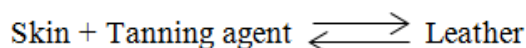


Figure 2. Time vs $\text{Cr}_2\text{O}_3\%$ of process bath for trial variations

A method used when working with a chemical reaction – and tannage must be considered as such, as illustrated here in a highly simplified form – may be considered particularly environmentally friendly when the reactant is transformed completely:



However, 100% conversion of a reactant is not possible. To allow the complete conversion of at least one of the partners, the quantity of the other one is increased, i.e. it is offered in excess. In the case of chrome tannage, this means that there always remains a residual quantity of substance in tannage float. By improving the reaction conditions, for example by increasing the concentration via a shorter float and increasing the final temperature and pH, it is possible to enhance the conversion process and reduce the quantity of surplus chrome tanning agent, provided this is permitted by the leather quality (Germann 1995)

When Figure 2 is considered, the best exhaustion of chromium takes place in trial A2B2, which is heating up to 40°C and starting basification in the middle of tanning process. A3B1, A3B2 and A3B3 trials which a heating process is applied at the end of the tanning process also gave better results comparing to other trials. It can be said that, increasing the final temperature of chromium tanning process enhances tanning reaction and gives better exhaustion of chromium in the bath.

Uptake of chrome is closely dependent upon temperature. After the shrinkage temperature had been safely increased in the first stages of a chrome tanning system, it was shown that temperature elevation improved both the uptake of chrome and the uniformity of leathers manufactured. Small pH changes can have a significant effect on the chrome uptake at lower tanning temperatures, but have a reduced influence at elevated temperatures (Daniels 1994).

From the Figure 2, it is seen that a certain amount of chromium oxide up to 30-40% remains in the process bath at the end of the process. Heideman (1993), states that it is a characteristic of these reactions that they approach equilibrium slowly, so that complete exhaustion never happens. If 100% float is used with an offer of 2.5% Cr_2O_3 , maximum exhaustion is about 80%. Use of shorter float and lower chrome offer promotes efficiency, but cannot alter the equilibrium thermodynamics.

Shrinkage temperature implies the hydrothermal stability of leather and it is commonly related with the degree of tanning (Mutlu et al. 2014). An important feature of chromium tanning is the ease with

which high shrinkage temperatures can be achieved; typically, 110°C is reached with 3% Cr₂O₃ in the leather (Covington 1991).

Figure 3, shows the shrinkage temperatures of blank and the trial leather samples. The shrinkage temperature of the blank sample was found 115 °C. The shrinkage temperatures of trials have been found almost the same or higher than the blank sample. The highest shrinkage temperatures were obtained for A3B1, A2B2, A1B1 and A2B1 trials which were around 120 °C. From the data we can say that early basification time has positive effect on increasing the shrinkage temperature of leather.

Under the imposed conditions of constant temperature, pH and chrome concentration in the tanning liquor, it was shown that changes in the temperature or pH do not have equivalent effects on tannage. The dominant effect of temperature is on chrome fixation. But tanning at higher pH on equal chrome content basis is more effective in raising the shrinkage temperature than higher temperature. (Covington 1991).

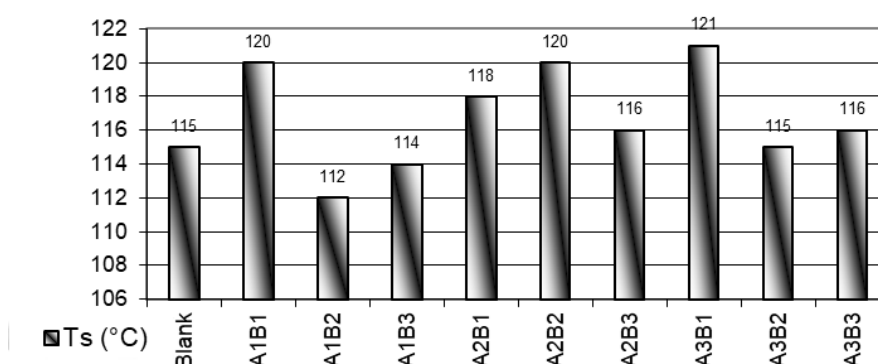


Figure 3. Shrinkage Temperatures of trials

The minimum chromium oxide limit for finished leather is suggested as 2.5% (UNIDO 1996) and the samples tanned with chromium in this study contain Cr₂O₃ confirming with this limit value as seen in Figure 4. From the graphic, it is seen that chromium oxide contents of leathers have been increased by the heating application at the middle or end of chromium tanning process. This confirms the dominant effect of temperature on chrome fixation.

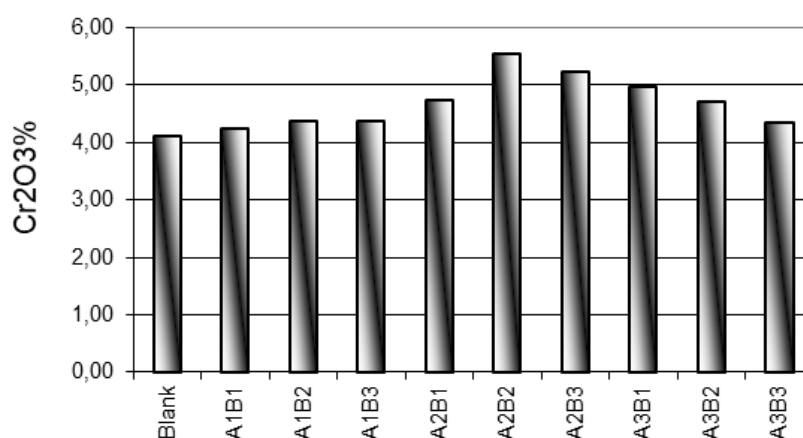


Figure 4. Cr₂O₃ contents of leathers

After monitoring the chromium uptake, chromium oxide contents and shrinkage temperatures of leather samples; wet-end processes were carried out in one batch according to a standard garment production route. Physical properties of the finished leather samples were investigated by physical tests and the results of tensile strength, elongation % and tearing strength are given in Figure 5, 6 and 7.

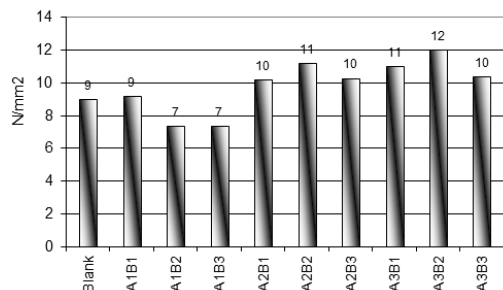


Figure 5. Tensile strengths of leather samples

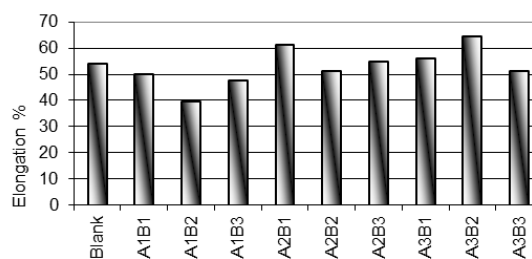


Figure 6. Elongation %s of leathers

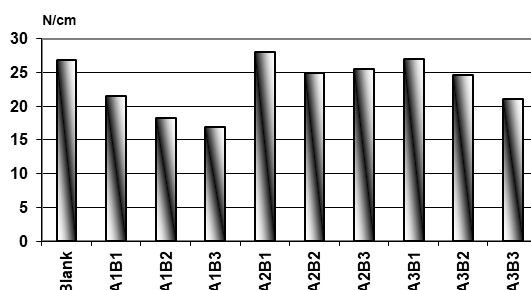


Figure 7. Tearing loads of samples

UNIDO guidelines advice a minimum of 10 N/mm tensile strength and 15 N/mm tearing load for chrome tanned garment leathers (UNIDO 1996). When tensile strength data of leather samples are considered, it is seen that blank sample and early heating trials are just a little below than the recommendations. However by heating application at the middle and end of chromium tanning process, an increase at the tensile strengths were observed and this was also valid for elongation % data. Considering the tearing loads of leather samples, all were higher than the recommended values. Again early heating parameter gave the lowest tearing loads.

4. CONCLUSIONS

From the resulting data of this study, the following conclusions were obtained:

- When the chromium content of tanning bath is monitored during the process time, the main exhaustion takes place in the first 30-60 minutes.
- Increasing the final temperature of chromium tanning enhances tanning reaction and gives better exhaustion of the chromium in tanning bath, thus better chromium uptake of leathers.
- Increasing temperature of chromium tanning in middle or at the end of the tanning process enhances physical strength properties of final leathers.
- Early basification times have positive effect on increasing the shrinkage temperature of leathers.
- Considering the trial parameters of this study, best chromium exhaustion took place for the heating in the middle of tanning and mid basification parameters.
- Spectrophotometric online monitoring of tanning process could be a good way of following and optimization of the process.

Computer assisted operations in leather processing have benefits of savings in process time, enhanced chemical uptake, uniform chromium distribution in leathers, overall improvement in leather quality and consistency and reduced load of pollutants in effluent streams. Chemical and water additions, drum revolution, pH and temperature are controlled by computers (Muralidharan 1995 pp 92). Spectrophotometry and online monitoring of chemicals can be also implemented in computer assisted production.

By monitoring the chromium concentration in a tanning process the chromium uptake can be made more uniform. Also the continuous adjustment of chromium uptake by chemical additions to the optimum level will improve the uptake. As a result more uniform and better quality leather is obtained besides possible chemical savings (Marjoniemi 1995).

However one drawback of implementation of spectrophotometry in process monitoring is that any chemical which can change the colour, concentration, temperature and pH in major units can distort the measurements. This study was conducted at laboratory scale and with minimum chemicals.

Landmann (1991), states that UV/Visible Spectrophotometry has also been suggested for estimation of chrome exhaustion and effluents. These determinations can be subject to interference, as the colour can differ with pH and other materials in float.

Marjoniemi (1995), also agrees that the calibration models can only be applied to samples falling within the concentration, temperature and pH ranges and the same chemicals as those used in the calibration samples. The most important thing in making the samples for a chromium calibration model is that they must resemble as much as possible the different compositions and situations there may be in the tanning process.

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