A Research on a New Chrome Tanning Agent

Asım Öncüler*

*TDT Consulting Ltd. Inc. Sureyya Agaoglu sok. No: 29 Da:4 Tesvikiye, Istanbul / Turkey, +902122338844, asimonculer@yahoo.com

Abstract

In this study, the effects of a new Basic Chromium Sulphate (BCS) based new chromium tanning product (NCTP) which is recently developed by us and produced by Kromsan, is discussed. It is known that classical BSC has the ability to bind onto the leather to a certain level and unbound chromium passes to the wastewater and to the sludge. NCTP, on the other hand, is bound onto the leather at a higher level resulting lower Cr content in wastewater and sludge also. In large scale tanning trials, it is observed that the leather grain is tight and smooth, full and round especially on the bellies. In addition to its positive physical properties, it has a better area yield compared to the traditional leather. In preliminary studies, its observed that the leather had a hard touch and leather dries too fast. These negative results have been solved by taking precautions during deliming, bating, retanning and fatliquoring.

With NCTP, the routine procedure of tanning will change. Because there is no requirement of pickling and basification, so no acid, salt and alkali addition is necessary. There is only a need for a light pH adjustment during neutralization. This enables tanning to be more cost-effective and reduces the detrimental effects for the environment.

This new tanning method is currently in progress in some tanneries for the production of shoe upper and double face leathers at large scale. We are working on the extension and familiarization of this method in all leather industry.

Keywords: chrome, tanning, clean production, chromium tanning, ecological

Introduction

It is widely known that chrome tanning has been introduced to researchers by Freidrich Knapp's article, "On the nature and essential character of the tanning process of leather" in 1858. However, there have been some studies predating the publication of this article primarily by Thomson (1985). The application of this process dates back to Schulz's 1889 patent (US Pat.291784,1884) employing the two bath method. Following this, in 1893 Martin Dennis got a patent utilizing the single bath method. If we consider that the two bath method is no longer being used, we can say that the origins of chrome tanning began in 1893. There have been some vast advances in chrome tanning in the last 120 years and today up to 85% of all leather production use the chrome tanning process (Luck, 1986). Beginning in the 1970s, there have been increasing discussions of the environmental consequences of chrome tanning (Germann, 2011). There have been efforts to decrease the environmental problems associated with chrome tanning as well as attempts to develop alternative materials and methods. However, there has been no satisfactory progress on these fronts in the last 40 years.

The chrome tanning materials we have developed provide a solution to these problems in an economically efficient way (Onculer, 2009). Our trials utilizing this material have proven that this a very viable product. This new chrome compound is called NCTP and has been produced and made available for the market by Soda Sanayi Ind. Inc.

The new chrome compound differs from traditional chrome tanning procedures on three accounts.

1. There is no need for pickling,
2. The chromium compounds penetrate leather at ph 6-7 and they can fix on the leather during tanning process,
3. There is no need for basification.

These three points signify important innovations in terms of tanning materials and tanning procedures. While there had been studies on tanning at higher ph levels without pickling in the past, these lacked the possibilities offered by the new compound and hence have not gained a wide appeal.

We have observed that the new chrome compound can successfully be used at an industrial scale with various types of leather. We provide the results of studies on shoe upper leather in trial drums and later at the Sepiciler Leather Ind. Inc. We have observed that this application provides a better chrome fixation. In addition, because there is no longer need for pickling, the amount of salt in sludge has reduced to a more environment friendly level. Also, the new tanning method has a higher area yield and does not require pickling and basification which results in abandoning the use of salt, acid and magnesium oxide. Moreover, the new compound provides economic advantages such as the reduction in material usage in neutralization and retanning. However, it must be mentioned that some adjustments in fatliquoring and retanning are required.

Material and Methods

In this study, we have used a newly developed BCS based tanning product NCTP named after its ecological benefits. NCTP contains 17% Cr_2O_3 and has 24% basicity. In these trials, we have used hides for shoe upper leather that weigh about 30-32 kilograms. The main method we have used for tanning trials could be summarized as follows:

First, traditional procedures were followed in soaking and liming the hides. After lime - splitting, full de-liming was applied. This was followed by normal bating where the pH level was around 7. A suitable surface active material was used to wash the pelts followed by the tanning procedure. Here is an outline of the tanning process:

- 40-60% Water at 25 degrees Centigrade
- 0.5% Oxazolidin at 15 minutes
- 0.5% Surface active material stable to BCS
- 0.5% Dicarboxylic acid at 90 minutes

- 5-7% NCTP at 8-10 hours
- pH: 4.1 (in leather) and 4.2 (in bath)
- Drain and wash x 2
- Sammying

The main difference with traditional chrome tanning methods is the use of pre-tanning. In this new procedure, the preliminary pH is conceived to be 6-7 so how to bring the leather to this pH requires an important consideration. It is not possible to guarantee full de-liming and bring the pH level as close to 6 as possible with the use of ammonium salts. In addition. It has been found appropriate to use 0.5 % Oxazolidin to increase safety (Kai, 2009). All analyses concerning the physical and chemical attributes of leather and waste are carried out in accordance with “Methods of Analysis” (SLTC, 1996) book.

Results and Discussion

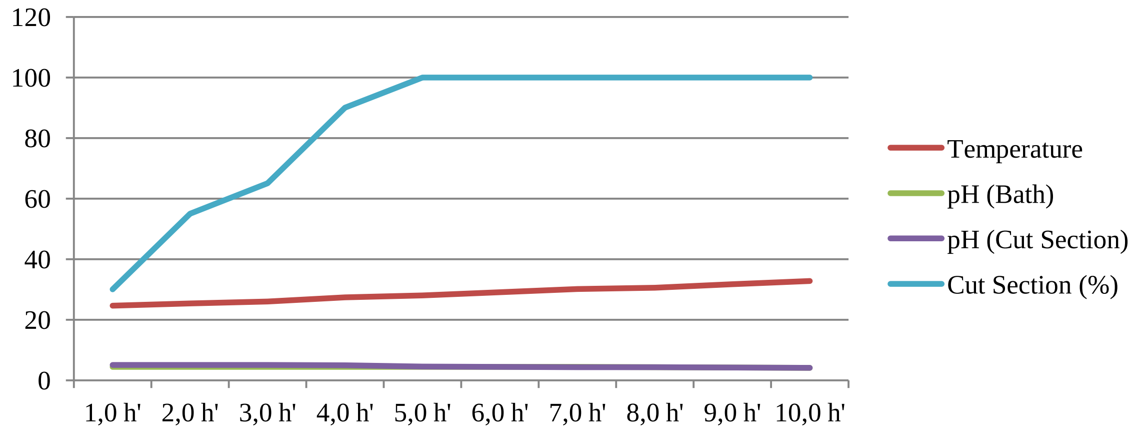
In this study, we offer a new tanning process as an alternative to the traditional tanning procedures as well as investigating the environmental effects of chrome tanning. Initially, we observed time based temperature change, change in bath and cut-section pH and change in penetration levels. You can see the results in Table 1.

Table 1. Variation of temperature, penetration, pH at bath and cut-section with time in tanning trials

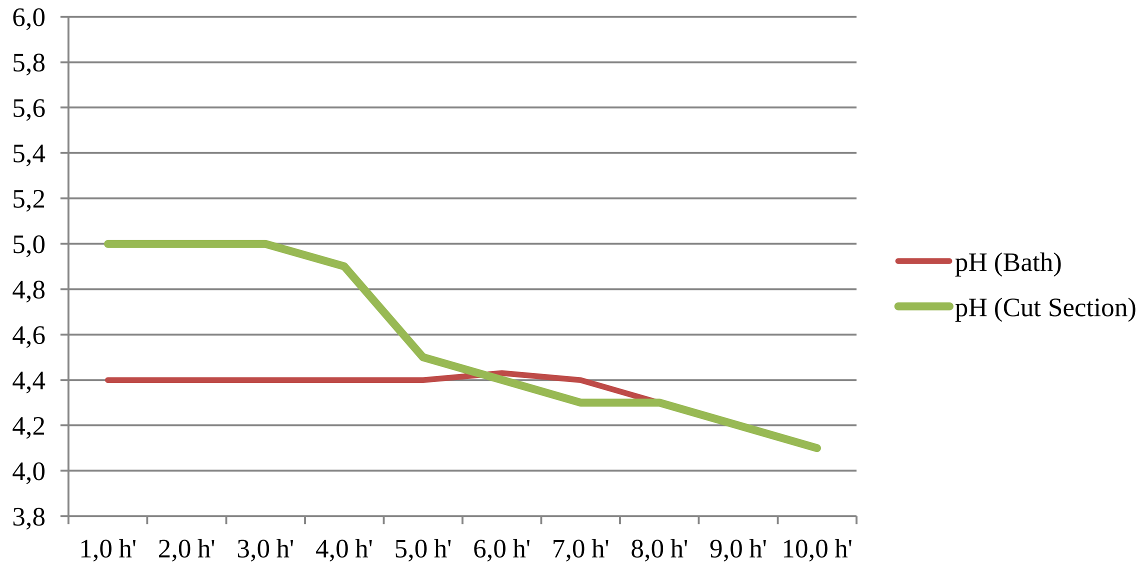
Time (hour)	Temperature (^{0}C)	pH (Bath)	pH (Cut-section)	Penetration (%)
1	24,6	4,4	5	30
2	25,3	4,4	5	55
3	26	4,4	5	65
4	27,4	4,4	4,9	90
5	28	4,4	4,5	100
6	29	4,4	4,4	100
7	30,1	4,4	4,3	100
8	30,5	4,3	4,3	100
9	31,7	4,2	4,2	100
10	32,8	4,2	4,1	100
9	31,7	4,2	4,2	100
10	32,6	4,2	4,1	100

As you can see from the table, during the tanning process, the drum was opened hourly to make the controls. The tanning temperature which was 24.6 degrees at the beginning rose up to 32.8 degrees due to the mechanical effects of tanning. Hence it was observed to be 32-33 degrees at the end of the tanning process. Th pH levels for both bath and cut section have been monitored and it has been recorded that the pH of cut section dropped to 5 from 6 in the first hour and was observed to be 4.4 in bath . Taking into consideration possible deviations caused by the experimental design, it can be seen that the pH levels of float and pelt are about the same. The chrome penetration level which was 30% at the first hour, reaches 90% at hour

4 and 100% at hour 5. In order to guarantee full tanning, duration of tanning process extended to 10 hours regardless of the 100 % penetration. If we compare this to traditional tanning procedures where pickling and tanning last for 20 hours, the time of the procedure has been reduced to half.



Graph 1. Variation in temperature, bath pH, cut-section pH and penetration



Graph 2. Magnified version of bath and profile graph

As can be seen in Graph 1, while temporal change and pelt penetration can be fully observed, the pH levels of float and pelt almost overlap. We can observe the relationship between float pH and pelt pH and note how they differ in Graph 2. If we consider Table 1 and Graph 2, we can note that there are no observed differences between float and pelt pH levels until the penetration is complete. With fixation, there is an observed decline in pH levels.

After the tanning process, the leather has been sammied and sorted according to their qualities. Observations during the samming process reveal that the leather grain is tighter, is more homogenously tanned and that there is no drawn grain or stains on the surface.

Controls during this process reveal that shrinkage temperatures rise to 116 degrees.

In the wet blue analysis, a more homogenous chrome distribution is observed both on surface and on pelt compared to the classical methods. The amount of Cr_2O_3 in leather and sludge show that goals have been met both with regards to the quality of leather as well as the environmental objectives. The chrome distribution in the new method is more homogeneous compared to the classical one as you can see in Table 2.

Table 2. Comparison of Chromium distribution in standard chromium and NCTP tanning

	Chrome (BCS) Added : 7%		NCTP Added : 5%	
Leather Layers	**Chromium Content**	**Chromium Percentage (%)**	**Chromium Content**	**Chromium Percentage (%)**
Grain Layer	4,03	40	3,49	34
Mid Layer	2,52	25	3,38	33
Flesh Layer	3,6	35	3,48	33

This study also focues on the cross sectional chrome distribution. We conducted chrome analysis at three layers: grain layer, mid layer and flesh layer. The amount of chromium oxide was observed to be 3.49% at the grain layer, 3.38% at the middle layer and 3.48% at the flesh layer. When compared to the traditional tanning mechanisms, NCTP results in a more homogenous distribution of chrome among layers. This is understood to be an advantage of the new procedure. We have also studied the amount of chrome oxide in float which was measured at 0.22 g/L Cr_2O_3. When we compare the Cr_2O_3 levels of the grain layer with the middle layer, we observe a more homogenous distribution than traditional methods. The main reasons behind this are the lack of basification and the ability of the newly formed compounds to penetrate leather at higher pH levels. No doubt this enables a higher area yield of approximately 2 % and the possibility of a finer grain.

The absence of pickling could also be considered from a practical perspective. As is well known, pickling causes losses in collagen substance (Bienkiewicz, 1983). When we consider that ice is added to the pickling bath on warm days, the new method yields a fuller belly part and a higher quality double face leather. On the other hand, from a practical standpoint, one could question why the double face leather producers store pickled leather. Leather produced with the new method is tighter. As pickling causes the removal of dermatan sulfate from the leather, it is inevitable that necessary adjustments be made to offset the effects of preliminary mechanisms (Alexander, 1986). Another effect of pickling is that the sodium chloride used with the acid reacts with the chrome compound and the resulting wet blue is made up of a chrome-sulfate-chloride collagen complex. The new compound however is made up of a chrome-sulfate collagen. These two structures undeniably yield different characteristics. Considering the complex structure of Wet blue in addition to the hydrotropic, hygroscopic qualities of sodium chloride and its ability to peptisize, it is necessary to use a suitable surface active material in order to prevent fast drying in the storage of wet blue. Fungicide which will be used in the storage of wet blue needs to be active above pH 4.

The relationship between leather and water must be considered carefully because of the difference in the complex structure of wet blue. The leathers processed with basic chromium chloride and BCS show their different character by the differences in the loss of water due to heat (Takenouchi,1981). Since water is one of the defining elements of leather, in the new application, this matter requires more attention (Reich, 2007). This was observed in preliminary studies as the leather treated with the new compound dries faster and more easily. In order to prevent this, we employed a different neutralization - fat liquoring method and materials to regulate drying.

Based on the type of the desired product, tightness could be seen as an advantage. In addition, with this new method, a new cationic leather is obtained. This could be an advantage for the darker colored dying process. Thus, one of the main handicaps for the anionic leather production is the attainment of dark colors. During the neutralization process, one should consider that the leather is more cationic. With the new compound, more positive results have been obtained compared to more traditional fatliquoring methods. Information on the levels of chrome oxide in float, chrome oxide fixed leather and chrome oxide in waste discharge is shown in Table 3.

Table 3. Results based on chrome bath in drum, leather and discharge

	IN DRUM					**IN LEATHER**		**IN DISCHARGE**		
	Hide Weight (kg)	Cr Powder Percentage (%)	Cr Powder Amount (kg)	Cr_2O_3 Amount (kg)	Float (l)	Fixed Cr_2O_3 (%)	Cr_2O_3 Content (%)	Total Cr_2O_3 (kg)	Total Cr_2O_3 Percentage (%)	Cr_2O_3 Concentration (g/l)
Standart Chrome	4500	6	270	70,2	2700	80,8	3,6	13,5	19,23	5
NCTP	4500	5	225	38,3	1800	99	3,6	0,4	1,04	0,2

As can be observed from the table, the amount of chrome fixed to leather remains the same, the quantity of chrome in the waste float decreases considerably. This is an important advantage of the new method. The increase in the fixation of the chrome to the leather decreases the chrome oxide amount in the sludge. As is well known, the chrome oxide amount in the sludge of the normal purification system is 17,000 - 20,000 ppm. According to the current code, this value should be below 1,000 ppm. This is initially lowered to nearly 6,000 ppm but this is still much higher than the required limit for the sludge (Akinci et al., 2013). 0.22 g/L chrome oxide mentioned in the purification in the above process produces a result of a reduction under 1000 ppm chrome in the sludge. This shows that chrome will no longer be a problem in the sludge. This result obtained as a result of this study is extremely successful and satisfactory.

The essential point of the research is the comparison of properties of traditionally and NCTP tanned leather and the results are shown in Table 4.

Table 4. Properties of leather tanned with standard BCS and NCTP

Properties	Standard BCS	NCTP
Shrinkage Temperature (°C) (above 100 °C)	No Shrinkage	No Shrinkage
Water penetration (2h)	None	None
Water absorption (%)	11,9	9,17
Tensile strength (N/mm²)	19,23	24,3
Extension (%)	40,57	48,51
Tear Strength (N/mm)	14,51	15,27
Lastometer (mm)	7,09	9,11

Conclusion

The conclusions of the study can be summarized as follows:

The benefits of the use of the new chrome compound in tanning,

1. It brings an environmentally viable solution to the chromium problem,
2. NaCl usage is not necessary in the process,
3. Significant increase in area yield,
4. Improves the quality and characteristics of leather,
5. Does not require any additional change or investment on process,

In addition to these advantageous results, it presents some differences to traditional methods particularly with regards to the application;

1. The m-alkaline test of the water used should be carefully applied
2. Before tanning, the pH level of the hide should be homogenously brought to pH 6-7
3. Fungicide (functional between pH 2 and 7) that is effective above pH level 4 should be used
4. During the tanning process, a suitable surface active material should be used
5. There should be adjustments made to the neutralization and fat liquoring processes.

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