Paper B9

Transformation of pelts to wet blue, without basification and high chrome exhaustion.

José Mª. Adzet
Research Association of Tanning Industries and Annexes –AIICA-, Avda. Pla de la Massa, s/n., Igualada, Spain, Tel. +34 938055388, Fax +34 938050618, e-mail: info@aiica.com

1.-Introduction

In a lecture presented at Barcelona IULTCS Congress in 1991, an interesting bibliographical summary is provided on the chrome tanning (3). After the process of chrome tanning in strict sense, it gets used to adding a basification agent in order to get the bath exhausted of chrome salt.

The addition is realized when remain few chrome salt in the bath and the modification of the pH start in the solution that moistens the external surfaces (grain and flesh) of the hide, where there is fixed a major quantity of basic chrome than inside of it. This way of procedure gives an unequal distribution of chrome in the skin and, even it, can form spots on the grain.

The aim of this research carried out with bovine pickled hides at diverse pH, consists in tanning them with different percentages of high basification chrome liquor, obviating the operation of the basification and to validate the efficiency of the tanning process. The main problem found is to obtain a chrome liquor of high basification, avoiding a mixture of products .

An exhausted bath and a wet blue hide with a TS nearly of 100ºC is obtained. Later the wet blue has been transformed into articles of high quality destined to upper leather for footwear. It is of highlight the uniformity of the dyeing and the feel of the skin, which confirms that the new process is trustworthy.

The chrome tanning process without basification is a simple system that has been carried out without problems. It comply with the environmental requirements for residual baths of chrome tanning ; and the quality of the obtained wet blue allows to make articles of high quality.

Pickle pH.

The pK of the carboxylic groups of the skin, on which the chrome aggregates are coordinated, is about a value of pH 4 (1). That is to say, at this pH value a half of the carboxyl groups are ionized. At higher pH values will be more carboxyl groups ionized and the hide will be capable of coordinating more chrome aggregates. At lower pH values, we shall have fewer carboxyl groups ionized and the hide will be less capable to react with chrome salts.

The Beaumè graduation of the solution over 4’5ºBé avoids the hide fibers swelling, facilitating the penetration of the bath to the inner part of the hide, which takes place by diffusion and mechanical effect across the inter-fibers spaces, which are big enough to let the penetration of the basic chrome liquor.

Once introduced the chrome salt aggregates inside the hide, it is needed some time to let them to react with the ionized carboxyl groups and to stabilize the hide, that is to say, to increase the shrinkage temperature .

The normal chrome tanning operation takes between 6 and 14 hours, including the basification process.

Chrome salt basicity.

The chrome salt without basification does not fix on the reactive groups of the hide and consequently it goes through in the hide easily.
By increasing the basification of chrome salt also increases his astringency, becoming insoluble for basifications higher than 60 % without masking. The stability of a basic chrome salt is increased when it is masked.
The chemical industry mainly produces basic chrome salts of 33 % and 45 %. The basic solutions of chrome salt needs time for olation and to form aggregates. As higher be the basification, major will be the aggregates that can reach colloidal size.
Having dissolved a solid chrome salt, it becomes ionized giving aggregates of negative load that, with the time, turn into positive due to the sulfate groups goes out from chrome complex (2) towards the bath.
The tanning in strict sense, consists in stabilizing the collagen structure by forming multiple links between different fibers . The native hide at neutral pH has Ts of 62ºC, whereas the chrome tanned hide reaches easily values over 100ºC, which can be verified simply carrying out the boiling test during two minutes. The hide well chrome tanned does not suffer any type of contraction during the boiling test, but if its tanning is deficient , the hide will shrinks and twists.

Standard tanning of bovine hides with basic chrome salt.

By a standard chrome tanning process, after the deliming and bating operation the pelt is pickled at pH values between 3 ' 4 - 3 ' 8, trying that the cut remains uniform, with bath salinity about 5 - 6 º Bé.
Then, solid basic chrome liquor at 33 % is added directly to the drum and it runs until the hide becomes crossed by chrome, which is evaluated by the bluish color of the hide section.
Later we add a basifying agent, which aim is to reduce the acidity of the bath and to achieve a major hydrolysis of the chrome salt, which increases its astringency for the hide.
There are so many tanning processes as chrome tanneries. The type of wet blue obtained in different factories will depend of:

- The beamhouse process to which the hides has been submitted.
- The characteristics of the pickle.
- The quantity of chrome salt used and its basification.
- Quantity and temperature of bath, drum revolutions and running duration .
- Quantity and type of basification agents used.
- Washed or without washing.

Dynamic of basification process.

Once the basic chrome salt has crossed the hide section, a part of the bath acidity must be neutralized to achieve a better exhaustion of the chrome, adding a basification agent that should allow to reduce the chrome concentration of the bath up to 0 ' 2 % of Cr2O3, or less.

The basification agents can be insoluble, as magnesium oxide, or soluble as sodium bicarbonate. Magnesium oxides, with different crystallizations as well as different particles sizes, can be found on the market.

The basification process take place at 40ºC in order to better neutralization of the bath acidity, produced by hydrolysis of the chrome salt.

The sodium bicarbonate, beside neutralizing the acidity, forms complexes with the chrome aggregates increasing its stability.

When you add the basification agent, it neutralizes the acidity of the bath and the superficial layers of the hide also, whereas the inner of it remains more acid. By this reason a major quantity of basic chrome can be fixed on the external layers of the hide enhancing the grain fragility. It is better to realize the addition of the basification agent in several times, instead of only one. The acid must go out of the inner part of the hide towards the bath, which is the place where the acidity is neutralized.

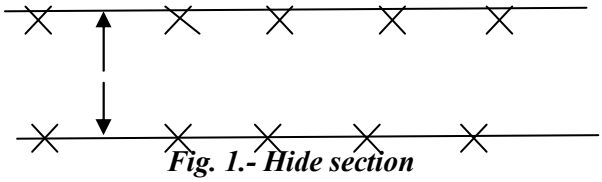


Fig. 1.- Hide section

When not all particles of magnesium oxide are dissolved, some of them remain adhered on the external layers of the hide, which are capable to form spots of basic chrome.
To avoid this problematic, we suggest to carry out the chrome tanning using chrome salt basified and olated, avoiding the operation of basification during the tanning process. The purpose of this procedure is to obtain a regular and uniform chrome distribution in the whole wet blue section.

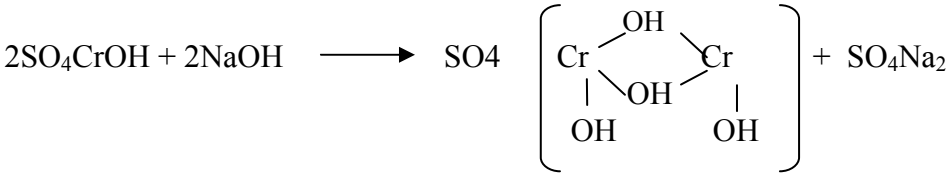
Preparation of salt chrome at 66% of basicity.

On the tanning sector market it is easy to find solid basic chrome salts of 33 and 45 %, but not with higher basification degree.
Since we wanted to work with a chrome salt of 66 % of basification, we had to prepare it by ourselves.
Starting from a basic chrome salt of 33 % it has been masked and basified up to 66 %.

Basic chrome sulfate 66 % solution

1000	Water
42	Masking agent
1158	Chrome Sulfate 33% basification (25% Cr_2O_3)
100	Sodium Hydroxide 50%
2.300	

The obtained liqueur has 44º Bé, pH 3'3 and its basification is of 66%, being its content of chrome oxide 12,6 % in weight.
During the basification process the solution is heated (neutralization heat). At the same time it is formed sodium sulfate that crystallizes by cooling the solution, as decahydrated.



To avoid the crystallization of the decahydrated sodium sulfate, the solution must be kept at 40ºC. The solution is left in rest for two days before using it in order that the phenomena of hydrolysis and olation of the chrome salt take place.

New process of chrome tanning.

In manufacturing process it is considered that the operations of deliming and batting are important since they allow to modify the characteristics of the hides according to the article to be manufactured.
The practical interest of the process consists in not using basification agents during the chrome tanning process and with it obtaining a uniform chrome distribution in the hide.

TANNING TEST WITHOUT BASIFICATION

To carry out this research have been used salted bovine hides from the country of 30 Kilos and submitted to the usual industrial beamhouse operations, to obtain upper leather for footwear. In the test "A" the pickle pH value have been left at 2'8 and in the test "B" to a pH 3,8 value.

Test A1

To carry out this trial bovine hides pickled at pH 2,8 are used; and the applied formulation calculated on the pickled weight are the following :

40,0 % Water
13,8 % chrome basic liquor solution = 1,74 g Cr2O3 = 7'0 g chrome salt
Run 2 hours
Checking : pH 2,81 / 9,1 ºBé and add
50,0 % Water
Run 4 hours
Checking: pH 2,80 / 6,1 º Bé

The hides rested the night on horse, after they are sammed and shaved . Later it has been realized a retanning, dyeing and standard fatliquoring, dried and mechanized.

Test A2

The hides used in this trial are pickled at pH 2,8 and the following formulation, calculated on the pickled weight of hides, are applied:

40,0 % Water
8,6 % Chrome salt basic solution = 1,1 g Cr2O3 = 4,4 g chrome salt.
Run 2 hours
Checking: pH 2,80 / 7,2 ºBé and add
50,0 % Water
Run 4 hours
Checking: pH 2,71 / 5,0 Bé

In the tanning process, significant differences are not observed in the penetration speed of the basic chrome liquor, but the bluish color of the wet blue is more intense in the test A1 which has major quantity of basic chrome liquor that in the test A2, which has less quantity of basic chrome liquor.
The hides rested on horse, having been sammed and shaved. Later it has been realized a retanning, dyeing and standard fatliquoring, dried and mechanized.
After running 2 hours with the chrome liquor and at the end of 4 hours, respective bath samples have been gathered from tanning bath to determine the residual chrome oxide in it.

Table 1. – pH, ºBè and chrome oxide contents on chrome tanning waste water

Determination	Standard	A1		A2	
		Checking 2h	Checking 4h	Checking 2h	Checking 4h
pH	---	2,81	2,8	2,8	2,71
ºBé	---	9,1	6,1	7,2	5
Chrome oxide in the bath (% Cr_2O_3)	IUC-8	1,2	0,5	0,7	0,3

Sample of the butt zone of the hides has been taken to determine the shrinkage temperature, as detailed in the following table:

Table 2. – Wet blue shrinkage temperature

Determination	Standard	A1	A2
Ts (ºC)	IUP-16	86,5	74,5

According to the values of the tables, the baths remain exhausted enough of basic chrome salt, but the shrinkage temperatures do not come to 100ºC. It is due to the small quantity of basic chrome liquor used , as well as the pH too much acid in the final tanning baths
By this reason it has been decided to carry out another test adding a major quantity of chrome salt and working with a pH of pickle less acid.

Test B1

In this test the skins were pickled to pH 3,8 and used the following formulation calculated on the pickled hide weight:

32,0 % Water
18,0 % Basic chrome liquor = 2,3 g Cr_2O_3 = 9,1 g Chrome salt
Run 2 hours
Checking: pH 3,38 / 11,1 ºBé and add

50,0 % Water at 35 ºC
Run 4 hours
Checking: pH 3,35 / 6,1 Bé

The hides rested the night on horse, and after are sammed and shaved. Later it has been realized a retanning, dyeing and standard fatliquoring, dried and mechanized.

Test B2

In this test the hides were pickled to pH 3,8 and used the following formulation calculated on the pickled hide weight

14,0 % Water
14,0 % Basic chrome liquor = 1,8 g Cr_2O_3 = 7,2 g Chrome salt.
Run 2 hours
Checking: pH 3,42 / 12,7 ºBé and add
75,0 % Water at 40 ºC
Run 4 hours
Checking: pH 3,40 / 5,3 Bé

The hides rested the night on horse, and after are sammed and shaved. Later it has been realized a retanning, dyeing and standard fatliquoring, dried and mechanized.

In the tanning process significant differences are not observed in the penetration speed of the basic chrome salt, but the bluish color of the wet blue is more intense in the test B1 which has major quantity of basic chrome salt that in the test B2, which has less quantity of basic chrome salt.

Table 3.- pH, ºBè and chrome oxide contents on chrome tanning waste water

Determination	Standard	B1		B2	
		Checking 2h	Checking 4h	Checking 2h	Checking 4h
pH	---	3,38	3,35	3,42	3,4
ºBé	---	11,1	6,5	12,7	5,3
Chrome oxide in the bath (% Cr_2O_3)	IUC-8	1,61	0,6	1,72	0,25

Table 4. – Wet blue shrinkage temperature

Determination	Standard	B1	B2
Ts (ºC)	IUP-16	98	98

In the test B have been used higher pH values of the pickle, as well as major quantity of chrome salt than in the test A, so it is obtained a Ts near to 100 ºC and the quantity of chrome salt in the residual final baths becomes reduced enough.
The test C is prepared to work with hides pickled to pH 5,7 and the quantity of basic chrome liquor added to the tanning process is of 12%, aiming to achieve a Ts higher than 100ºC and a residual bath more exhausted of chrome.

Test C

The test has been carried out using the splitted pelts, which has been pickled to pH 5,7 and the following formulation calculated on pelt weight :

25,0 % Water
12,0 % Basic chrome liquor; of 12'6 % Cr_2O_3 corresponding to = 6'0 % chrome salt
Run 2 hours

75,0 % Water at 40 ºC
Run 4 hours
Checking: pH 3,7 / 5,8º Bé TS > 98ºC

The waste chrome tannage bath have 0,1 % Cr_2O_3 and the leather 3,9 % Cr_2O_3 on dry weight.

DISCUSSION OF RESULTS

The penetration of chrome liquor of high basification into the hides, is achieved using a short bath of high salt content, higher than 10ºBé, which dehydrates strongly the fibers of the hides and increases the spaces between fibers.
Once achieved the total penetration of the hide, that in the case of splitted pelts is lower than two hours, the bath is basified adding warm water, in order to get a final tanning residual solution with low contents of chrome and saline concentration about 5'0ºBé.

With hides pickled to pH 5'7 it is possible to penetrate chrome aggregates of high basification, which particles are of colloidal size, which allows to obtain a Ts nearly to 100ºC and a finished leather of high commercial quality.
As no basifying agents are added to the chrome tanning baths, the distribution of the chrome in the hide is more uniform, without possibility that there takes place an over tanning of the external layers.

CONCLUSIONS

- A high basicity chrome liquor, that have big aggregates, can go through a pickled hide, without need of previous penetration with basic chrome salt of 33 %.
- Using chrome compounds of high basification, we can realize chrome tanning processes of high exhaustion without the addition of neutralizing agents.
- The most difficult thing is to obtain chrome liquor of high basification and keep them in liquid state.

BIBLIOGRAPHY.

1.-Chemistry and Technology of Leather.
O'Flaherty, Roddy, Lollar
Reinhold Publishing Corporation, Vol 2 (1956) New York
2.-Technical chemistry of Tannery
J.M.Adzet and others.
Romanya Valls (1985) Capellades (Spain)
3.-Chrome tanning without conventional pickle.
J.M.Adzet and others.
The XXIst Congress IULTCS - September, 1991 - Barcelona (Spain)
4.-Underlying principles in Chrome tanning: Part 1 Conceptual Design of Pickle-Less Tanning.
W. Legesse and others
JALCA 97 475 (2002
5.-Reduction of the conductivity in the baths of chrome tanning pickle.
E. Comes.And. You eat.
Leather Technology (AAQTIC) Vol. 22, 28 (2010)
6.-Green Chemistry Approach in Leather Processing: A case of Chrome Tanning.
M.P. Kumar and others.
JALCA 106, 113 (2011)