Innovating chrome tanning process with excellent exhaustion

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- Abstract

Over the last 30 years leather technology literature has been dominated by ways to reduce the environmental impact of leather production and techniques to reduce the discharge of chromium reagents have been a significant element in these endeavours.
At present, no tanning agent is able to replace completely the basic chromium sulphate in the production of all the articles range with a comparable quality, manufacturing cost and easiness of execution.
The chrome tanning processes based on partial replacement of chromium, are more realistic[(1)].
Consequently, in addition to the metal-free tanning, that complies with the request of a limited range of leather utilization, the research must be direct towards the improvement of the chromium fixation, by its using only in the retannage phase on the precedently pretanned hides.

- Unbound chrome in the wet tanned leather in conventional chrome tannage

Altough the processes for treating residual chrome tanning float (direct recycling or precipitation and re-dissolution) are apparently satisfactory, unfortunately they do not solve the problem of chrome pollution [(2)].
Infact at the end of a conventional tannage, carried out with an offer of 2000 g of Cr_2O_3 for 100 kg of hide, the tanned hides contain a significant amount of liquor with the same chrome oxide concetration of the residual float. If the ehausted float contains, for example, 5 g/l of Cr_2O_3, the liquor that can be squeezed out of the wet leathers will hold 5 g/l of Cr_2O_3. As 65% of its weight is made up of tanning float, absorbed during tannage, quite a considerable amount of unbound chrome is contained in it[(3)].
The quantities of unbound chromiun contained in 1 ton of leather, immediately at the end of tannage, can be calculated roughly in accordance with the formula in figure 1 [(4)].
According to this formula and to above mentioned assumptions, the quantity of unbound chrome is in proportional dimension with the concentration of chromium oxide at the end of tannage. Therefore the quantities of unbound chrome contained in the wet leather after tannage depend on the chrome concentration in the residual float at the end of tannage. In this case (5g/l Cr_2O_3 in the residual bath, 2000 g/100 kg of hides offered), the quantity of unbound chrome in 1 ton of the wet tanned leather is equivalent to 2,2 kg of chrome oxide. It means that about 11% of the total chrome offered is contained unbound in the wet tanned leather.
It is released during sammying, washing and retanning. From this, it follows that no far-reaching reduction in the chrome content of the effluent and sludge from tanneries can be realized unless the washing and retanning floats are also included. However, these floats cannot be smoothly integrated into the processes described above for treating the residual tanning floats because their volumes are too large for direct recycling. Precipitating the chrome out of the diluted rinsing and retanning floats poses technical problems and is virtually impossible in a tannery.
With a far-reaching exhaustion, the wet leather will also have a low content of unbound chrome tanning material and will therefore release accordingly small quantities of chrome during the ensuing operations.

Figure 1. – Formula for the rough estimation of unbound chrome in 1 ton of the wet tanned leather

$$x = 3/4 \cdot \frac{0{,}9 \cdot 650 \cdot y}{1000} = 0.438\ y$$

x	**=**	**kg of unbound Cr_2O_3/ton of hides**
650	**=**	**kg of bath contained in 1 ton of tanned hides**
0,9	**=**	**the weight of tanned hides is 90% of the weight of the fleshed weight**
y	**=**	**g/l Cr_2O_3 in the bath at the end of tannage**
3 /4	**=**	**the total quantity of unbound chromium (1/4 will be fixed in the hides before further operations)**

- Maximum exploitation of chrome used

This technology allows an excellent fixation of Chromium to collagen, owing to the modification of the chemical reactivity of the protein before beginning the chrome tannage**(5)**
The pickled hides, after conventional beamhous operations, are pretanned with an aldehydic substance. The pretannage is carried out in the pickle bath. Hides are shaved and then are tanned by using a conventional basic chrome sulphate.
The modification of the chemical reactivity of collagen, caused by the pretannage, promotes the start of chrome tannage to pH values between 6,5-7,0. In spite of that, the even chromium penetration through the whole hide section is achieved. The process, that foresees no basification, brings about the pH value of the bath, at the end of the tannage at 4,1-4,2. The neutralisation, at pH values according to the type of article (till 5,5-6,0 for upholstery leather) to be produced, is carried out in the same bath of tannage. The chromium precipitation does not take place owing to the very small amounts of chromium in the bath. After a washing , the leather is fatliquored, retanned and dyed.
This technology offers the following advantages :

- Well exhausted floats with scarce amounts of chromiun (Cr_2O_3 : 10-20 mg/l). It is possible to discharge the waste water effluents directly without any treatment.

- The shavings are chrome-free.

- The leathers show qualitative characteristics as feel, softness, fullness, firmness on the average higher as to those from conventional tannery production.

- Experimental

The following stages make up the process:

- Traditional beamhouse operation up to pickel stage.
- Organic products for pretannage: Ts of 75°C is reached, this aids shaving.
- Sammying out, splitting, shaving; splitting operation can be carried out both on pretanned or limed hides
- Chrome tannage : the amount of chrome oxide refers to shaved weight.
- Conventional following stages.

The processing cycle is made up of the stages according to the wheter options A or B are followed

Table 1.- Processing cycles

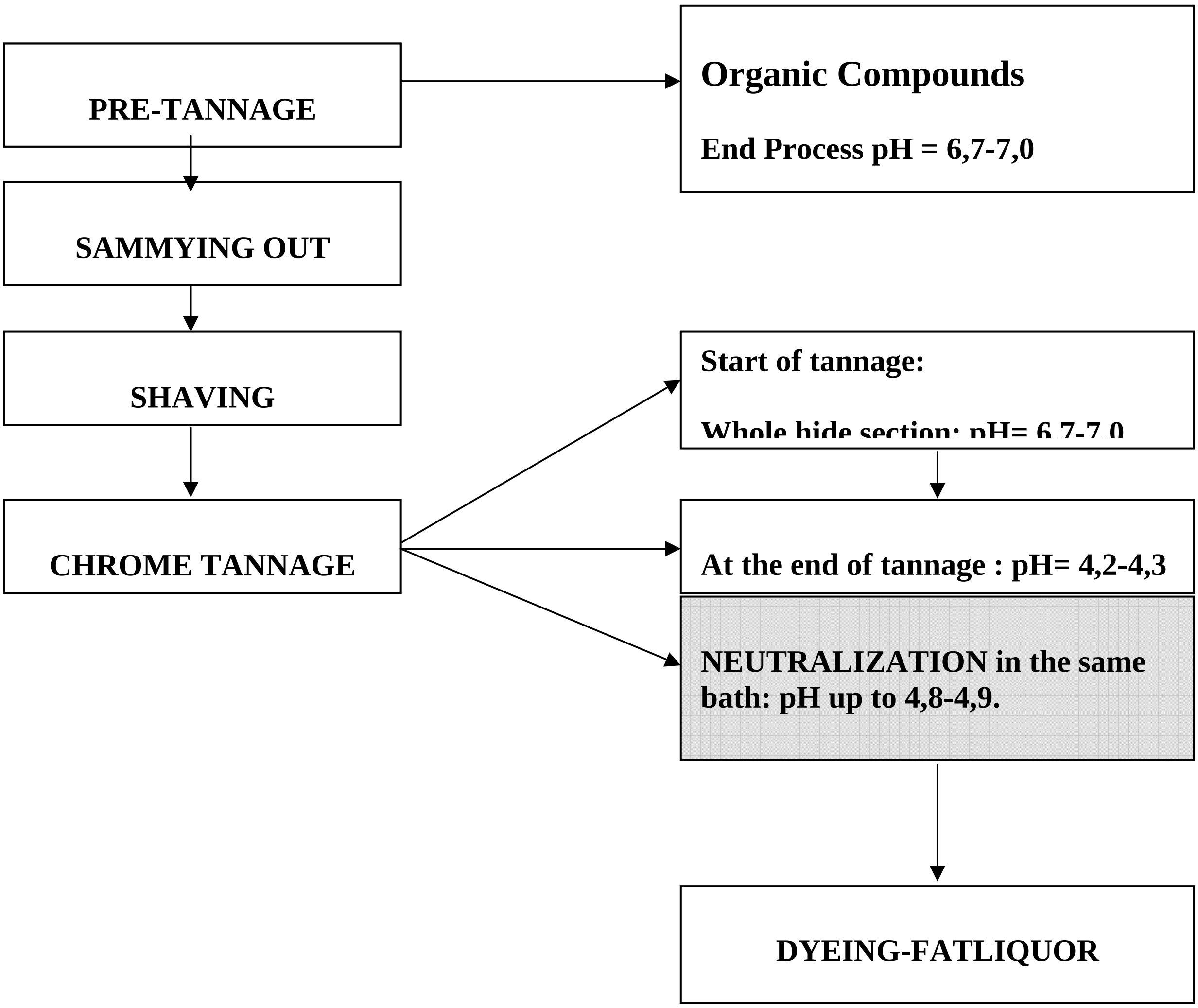
Process A	Process B
Soaking	Soaking
Unhairing-Liming	Unhairing-Liming
Fleshing	Fleshing
Splitting	Deliming-Bating
Deliming-Bating	Pickling- Pretannage
Pickling- Pre-tannage	Sammying out
Sammying out	**Splitting**
Shaving	Shaving
Chrome Tannage- Neutralization	Chrome Tannage- Neutralization
Fatliquor-Re-tannage	Fatliquor-Re-tannage
Dyeing	Dyeing

In order to enhance the process, three sets of trials were carried out.

First trial as per process A

Six greenweight,30-32 kg. bovine hides were soaked and limed and following fleshing and splitting they were processed according to conventional method up to the pickle stage (pH = 2,9 – 3.0). Pre-tannage with aldehyde compounds and synthetic tannins was carried out in the same float of pickel.

Figure 2.- Processing benchmarks: first trial diagram

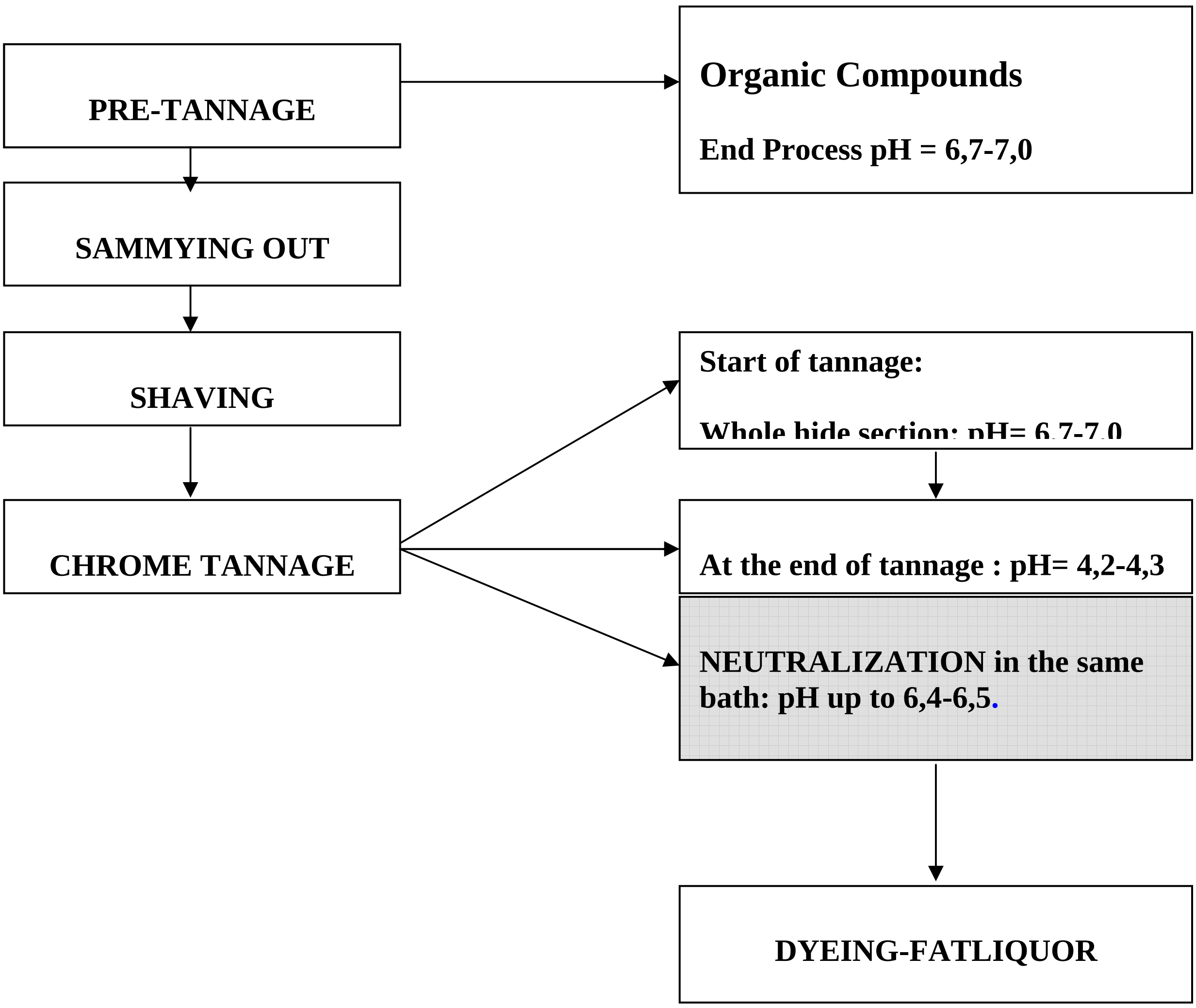


The pH reading at the end of pre-tanning was brought to a reading of 6,7 – 7,0. After sammying out and shaving the leathers were washed briefly in water at 30°C. The weight of the leathers after shaving to a thickness of 1,1 – 1,2 mm is about a third of the fleshed weight. Chrome tannage, carried out in the absence of a float, was carried out using 8% base chrome sulphate (25% Cr_2O_3 33% Bs) on shaved weight and 1% masking agent made up of sodium phthalate. Due to the observation made before, the amount of chrome referred to the shaved leathers equals about 1/3 of the amount referring to the shaved weight. After rotating for 60 minutes, 100% water was added at 30°C. After rotating for a further 60 minutes the pH reading of the float dropped to 4,2 – 4,3. At this point the very same float was neutralized with magnesium oxide based products up to 4,8 pH. Dyeing and fatliquoring were carried out in a fresh float. The leathers were analyzed to assess chemical-physical characteristics. The tanning float was similarly analyzed to establish the content of residual chrome oxide.

Second trial as per process A

Six greenweight bovine hides were processed in the same way as the first trial. The only substantial difference is shown by the fact that the final neutralisation pH reading following chrome tannage was brought to 6,4 while being carried in the same float as in the case of the first trial.

Figure 3.- Processing benchmarks: Second trial diagram

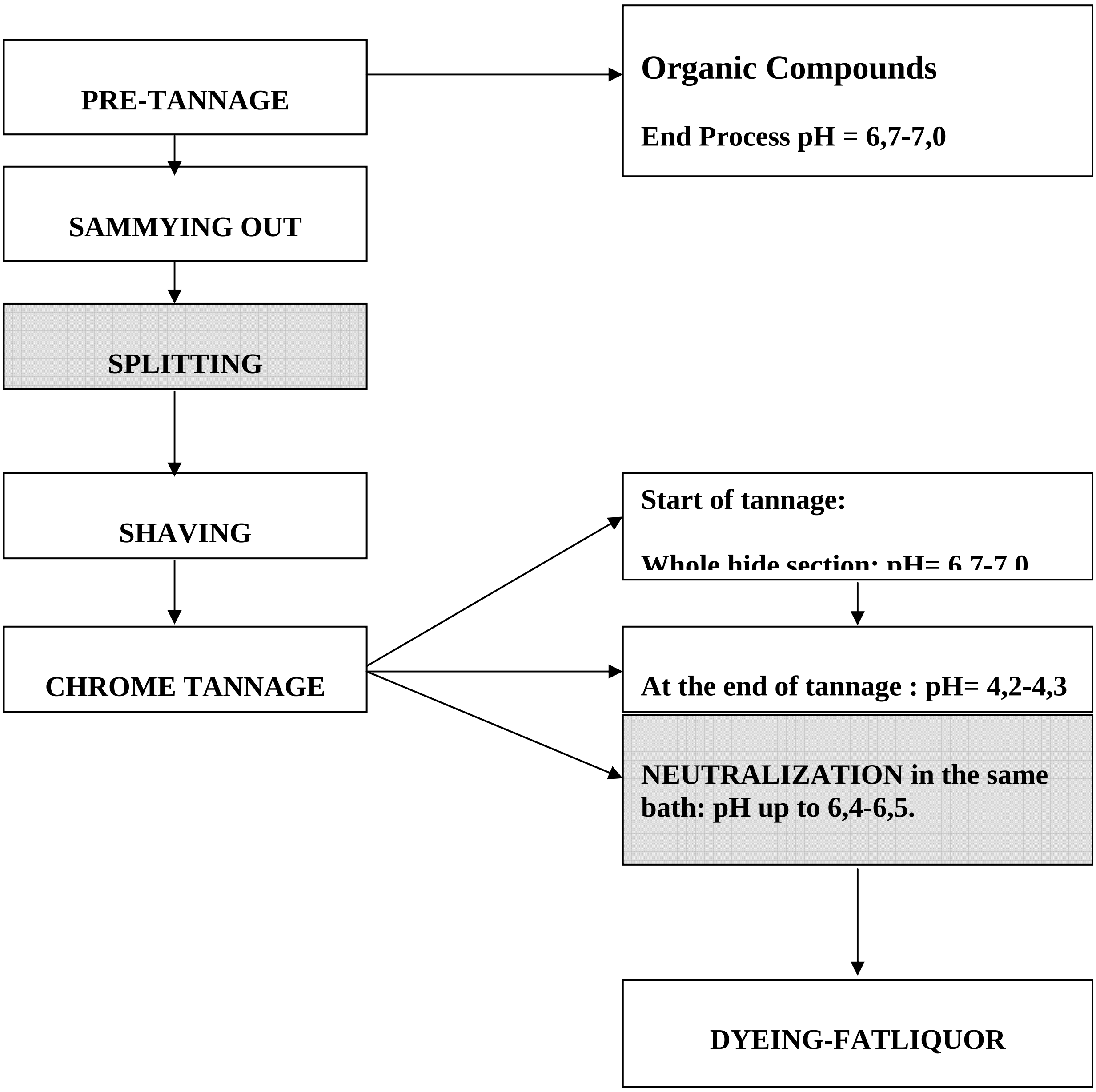


Even if the pH reading is very high, irregular deposits of chrome are not reported on hide surface nor is there coarsegrain. During the course of chrome tannage on pre-tanned hides using substances which can react with amino groups of collagen, even other researchers did not report chrome stains at pH readings which were clearly higher than traditional ones[(6)].
In these conditions there is such a high level of exhaustion that the chrome content is more or less negligible : furthermore, features of softness, fullness, grain firmness as well as mechanical-physical properties can be compared with those of tanned hides using conventional chrome processing methods.

Third trial as per diagram B

Six bovine hides from the same origin were processed in the same way as the second trial. The only difference was the splitting stage seeing as it was carried out after pre-tannage.

Figure 4.- Processing benchmarks: third trial diagram



- Results and debate

The following tables (2,3 and 4) show the chemical features of pre-tanned hides and those of leathers following chrome tannage as per each trial carried out and are compared with conventional chrome tannage characteristics (table 5). Even the chrome result: the degree of

chrome exhaustion in the final tannage bath, the amount of chrome oxide fixed in the hides with relative calculation of fixation performance can be seen in the same tables.
Chrome fixation performance is compared with hide substance. In the end an overall evaluation was made of mechanical-physical properties, the quality of leathers achieved as per the three systems previously described. Fullness, softness, and grain firmness were examined [7].

Table 2.- Leathers : first Trial, Splitting after Fleshing, end chrome tannage pH = 4,8

Assessment	Chemical composition of pre-tanned and shaved leather	Chemical composition of chrome tanned leather after shaving
Volatile matter (IUC 5)	69,5%	0,0%
Sulphated total ash (IUC 7)	1,3 %	10,0%
Hide substance (IUC 10)	28,5%	89,9%
Ossido di cromo (Cr_2O_3) (IUC 8)	--	**5,3%**
Cr_2O_3/hide substance . 100	--	**5,9%**
Shrinkage Temperature (IUP 16)	75°C	105°C

CHROME RESULTS

End chrome tannage bath pH reading = 6,5

Cr_2O_3 end tannage bath = 0,60 g/l

Cr_2O_3 fixed/hide substance . 100 = 5,9 %

Cr_2O_3 offered = 2,0/28,5*. 100= 7,0%

Fixation performance = 5,9/7,0 . 100 = 84,3%

* hide substance content of pretanned and shaved leather

Looking at the data shown in table 2, a high content of chrome oxide in the leathers can be seen. It is about 6% when compared with hide substance. The degree of exhaustion in the exhausted bath is quite good (0,6 g/l), whereas in the case of conventional tannage which is currently carried out industrially, it is not unusual to find readings of 5-6 g/l of chrome oxide at the end of processing. Conventional processing means a type of processing which, differently from the past, allows a higher degree of chrome exhaustion with the application of some measures such as short baths, high temperatures for a long period of the tannage stage (40°C), a reduced amount of chrome oxide offered, long tannage running time, higher pH readings (4,0 – 4,1). A higher temperature can be used as well as short float and longer running time whereas a higher pH reading and chrome reduction are not always compatible with the quality of some articles[8].
As can be seen in table 2, the process described allows much higher chrome fixation performance (about 84%), in comparison with conventional tannage.

Table 3 – Leathers : second Trial, Splitting after Fleshing, end chrome tannage pH = 6,4

Assessment	Chemical composition of pre-tanned and shaved leather	Chemical composition of chrome tanned leather after shaving
Volatile matter (IUC 5)	68,5%	0,0%
Sulphated total ash (IUC 7)	1,3 %	9,1%
Hide substance (IUC 10)	29,5%	90,1%
Ossido di cromo (Cr_2O_3) (IUC 8)	--	**5,82%**
Cr_2O_3/ hide substance . 100		**6,5%**
Shrinkage Temperature (IUP 16)	75°C	107°C

CHROME RESULTS

End chrome tannage bath pH reading = 6,4

Cr_2O_3 end tannage bath = 0,035 g/l

Cr_2O_3 fixed/hide substance . 100 = 6,5 %

Cr_2O_3 offered = 2,0/29,5. 100= 6,8%

Fixation performance = 6,5/6,8 . 100 = 95,5%

Negligible amounts of chrome oxide corresponding to 35 mg/l. stay in the residual and exhausted bath in this processing for which neutralisation is increased to a higher pH reading. The degree of exhaustion is extremely high. Both the amount of chrome fixed in the hides (0%moistness) as the degree of fixation performance are very high. Fixation performance refers to the relationship between the percentage of chrome fixed to the hide substance and the total offered which is calculated in percentage on the hide substance contained in pretanned and shaved hides.
Despite the fact that the pH reading at the end of tannage-neutralisation is so high, no chrome precipitation problems were found. No problems of chrome penetration or instances of precipitation were revealed with this technology.
The excellent degree of exhaustion and fixation performance which show high chrome reactivity towards collagen in processing conditions, do not affect penetration unfavourably, nor grain fineness or superficial deposits of the tanning matter.
The length of the tannage- neutralisation process (about 3 hours) is clearly less compared with traditional tannage and so, it is a further and by no means minor advantage.

Table 4 – Leathers : third Trial, Splitting after Pre-tannage, end chrome tannage pH = 6,5

Assessment	Chemical composition of pre-tanned and shaved leather	Chemical composition of chrome tanned leather after shaving
Volatile matter (IUC 5)	64,5%	0,0%
Sulphated total ash (IUC 7)	6,0 %	13,1%
Hide substance (IUC 10)	29,5%	86,8%
Ossido di cromo (Cr_2O_3) (IUC 8)	--	**5,85%**
Cr_2O_3/hide substance . 100	--	**6,70%**
Shrinkage Temperature (IUP 16)	75°C	>100°C

CHROME RESULTS

End chrome tannage bath pH reading = 6,5

Cr_2O_3 end tannage bath = 0,025 g/l

Cr_2O_3 fixed/hide substance . 100 = 6,70 %

Cr_2O_3 offered = 2,0/29,5. 100= 6,8%

Fixation performance = 6,7/6,8 . 100 = 98,5%

This process differs from the previous one only because hides are split after pretannage and results are basically confirmed even though the degree of chrome exhaustion as well as fixation performance are even higher.

Table 5 instead shows the chemical composition of chrome tanned hides and relative chrome result using industrial level conventional technology as has already been set out. The concentration of chrome oxide found in the residual bath corresponds to 5 g/l whereas fixation performance is about 50% while being calculated as in previous cases.

The comparison of these results basically points out marked advantages of the technology proposed

The process which envisages pretannage with aldehyde products and ensuing chrome tannage, effected in different pH interval compared with conventional tannage, allows exhausted floats which are more or less chrome-free.

Mechanical-physical benchmarks of finished hides compared with those shown by finished hides which were tanned using conventional tannage, reveal a slight reduction concerning tear and burst load fastness. On the whole it can however be said that mechanical properties are suitable for upper and upholstery leathers. Finally, finished articles display excellent features of feel, softness, fullness, and grain firmness.

Table 5. – Conventional chrome tanned hides

Assessment	Chemical composition of chrome tanned hide	
Volatile matter (IUC 5)	64,5%	0,0%
Sulphated total ash (IUC 7)	4,0%	13,3%
Hide substance (IUC 10)	28,5%	80,3%
Ossido di cromo (Cr_2O_3) (IUC 8)	1,66%	**4,7%**
Cr_2O_3/hide substance . 100	**5,85%**	
Shrinkage Temperature (IUP 16)	> 100°C	

CHROME RESULTS

End chrome tannage bath pH reading = 4,0

Cr_2O_3 end tannage bath = 5 g/l

Cr_2O_3 fixed/hide substance . 100 = 5,85 %

Cr_2O_3 offered = 1,75/15* x 100=11,7

Fixation performance = 5,85/11,7 x 100 = 50%

* Hide substance content of pickled hides

- Further Considerations and Conclusions

As is well known, the acidity of the pickling process cuts down ionisation of carboxylic groups and increases ionisation of amino groups. Thanks to these reactions, collagen reactivity is brought down against basic chrome salts enabling penetration. Basic ionized groups of side chains are not able to shift chrome hydrolysis equilibrium towards more basic forms which are therefore more reactive whereas the poor ionisation of carboxylic groups have poor affinity with the tanning compound. Based on evidence taken from the technology herewith, it seems that the chemical state of amino groups has substantial effect on the trend of chrome tannage.

Another way of influencing reactivity is to block basic functional groups of the polypeptide chain by making them react with aldehyde substances during pretannage.

As is known, optimum pH readings of collagen reaction with aldehyde goes from 6 to 8. In the method studied, chrome tannage starts from a pH reading of about 7 and then it is lowered by intrinsic acidity of chrome salt and stabilizes around 4,2 and 4,4. Basification-neutralisation then make end of tannage pH readings higher depending on the article desired. In this specific case trials were carried out using pH readings between 4,8 to 6,5. The higher the pH reading, the more carboxylic groups are ionized. Thus, compared with conventional tannage the technique referred to is carried out in a domain where carboxylic groups are mostly ionized.

Use of a masking agent in a very short float aids chrome penetration. Level distribution and at the same time a high degree of fixation of the tanning product are achieved.

Finally, it is possible to achieve finished hides featuring softness, excellent fullness, mechanical parameters within the norm with the technology under discussion. At the same time, negligible amounts of chrome can be found in final tannage floats.

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