Optimization of Tanning Through the Study of Different Tanning

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Abstract.
The major concern of humanity today is the care and preservation of the environment, the development of green technologies or process optimization has been the major focus of research. Based on these thoughts searched to improve traditional processes of leather industry for cleaner technology is mainly transform hides in leather similar or better quality to that which is already marketed. Aiming at improving processes regarding waste and leather quality, we searched a product that is compatible with other traditional tanning and a tanning efficient and mostly not generate a residue harmful to the environment or to humans. Through research aimed to the combination sulfate tetrahydroxy-methyl-phosphonium other tanning for evaluation of their use together in the tanning process or as a pre-tanning. The tests performed in this study were the combinations of basic chromium sulfate with tetrahydroxy-methyl-phosphonium and tannin with tetrahydroxy-methyl-phosphonium. An analysis of the baths residual calcium, total chromium, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids, total solids and hardness. In tanned leathers were performed the following tests: chromium oxide in dichloromethane extractables, calcium, retraction and light fastness. In the crust leathers were analyzed shrinkage, grain distention, tearing, light fastness, strength, aging, color fastness to perspiration and migration to PVC. There was obtained satisfactory results with respect to the bath exhaustion and quality of the leather, which were analyzed as can be concluded that the combinations with the tanning tetrahydroxy-methyl-and phosphonium basic chromium sulfate, and pretanning with tetrahydroxy-methyl-and phosphonium acacia modified tannin showed better results than reduced costs with respect to the basic chromium sulfate.

***Keywords**: Tanning, tetrahydroxy-methyl-phosphonium, environmental impact.*

1. Introduction

The process of the leather is very old and still very conventional and requires a lot of research for the emergence of new techniques become viable hides into leather. Thus, this paper proposes, through research, alternatives to make the process of tanning hides more efficient and sustainable.

The global market both as Brazilian leather has been growing over the years despite all the crises that comes through. According to the Guia brasileiro do couro (2012), the production estimate was 43 million hides the year 2011 with a herd of 205 million head of cattle. The share of the Brazilian market is 13.83% of the world market of leather.

Due to the great importance of the sector and concern about the impact of tanning this paper aims to:

- Propose formulations curtimentos less impactful,
- Comparing the different types of tanning through chemical and physical analysis and the hides in baths residual everificar the quality of the hides formed through physical testing;

2. LITERATURE REVIEW

According to the Tanner Vademecum (2005), the types of tanning split into tanning mineral and vegetable. Regarding to mineral tanning, has as main the chromium sulphate, but also are used aluminum and zirconium among others. The chrome at the tanning was solidified by the fact that it is a product that adds to the quality leather which encompasses physical-mechanical resistance, practicality of implementation, and cost competitive production versatility for different articles. (Naviglio et. al., 2011). According Pacheco (2005), in mineral tanning, the process is still the main chrome tanning process, used worldwide, the relatively short time of process and quality in leather which gives its main applications. Ocurtimento plant (the tannins contained in plant extracts) is generally used to produce soles and certain special types of leather, as well as in combination with other types of tanning.Naviglio *et. al.* (2011) comments that o processo de curtimento cromo solidificado por ser um produto que contribui para a qualidade do couro que abrange resistência físico-mecânica, praticidade de implementação, versatilidade e custo de produção competitivo para artigos diferentes.

The phosphonium salts are compounds introduced to the market little leather, containing in their molecule an atom of positively charged quaternary phosphonium. *Tetrakis-Hydroxymethyl Phosphonium Chloride (THPC)*, is the more known compound of this class, having the chemical formula shown in figure 1.

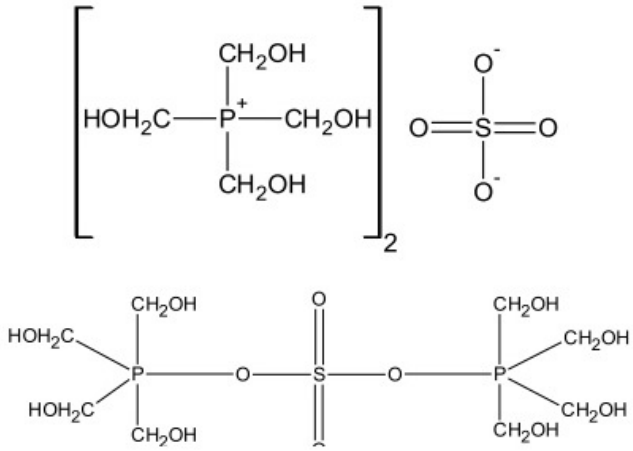

Figure 1. Sulphate Tetrakis-Hydroxymethyl Phosphonium Chloride (THPC).

Source: Naviglio *et. al.* (2011).

The THPS has a pH of around 4, being stable at pH less than 6, because at higher pH and / or slightly alkaline transformed into oxide trihydroxy-methyl-phosphine oxide (THPO) with formation of formaldehyde as Figure 2. The leathers produced with THPS at a temperature of 100 º C its retraction is around 25%, showing great bleaching, light fastness and perspiration. In the first phase of the tanning acid, THPS salt form exhibits low reactivity with the substrate and thus penetrates the section of hide with ease. With this penetration

finalized, the tanning is reactivated by raising the pH. This basification determines the formation of tri-hydroxymethyl phosphine (THP), which is the compound capable of insaturar crosslinks with the collagen, being able to see the presentation of this reaction in the figure 3(NAVIGLIO *et. al.* 2011).

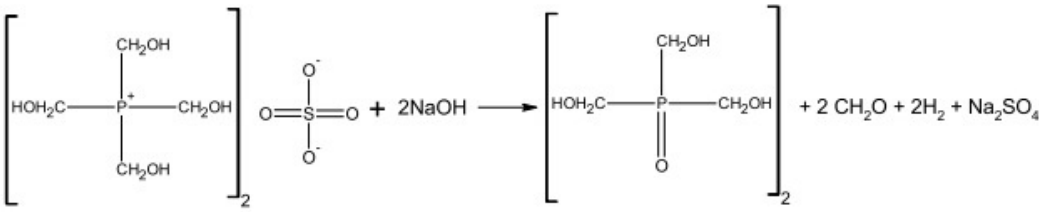

Figure 2. Transformation of THPS in THPO (tri-hydroxymethyl-phosphine).

Source: Naviglio *et. al.* (2011).

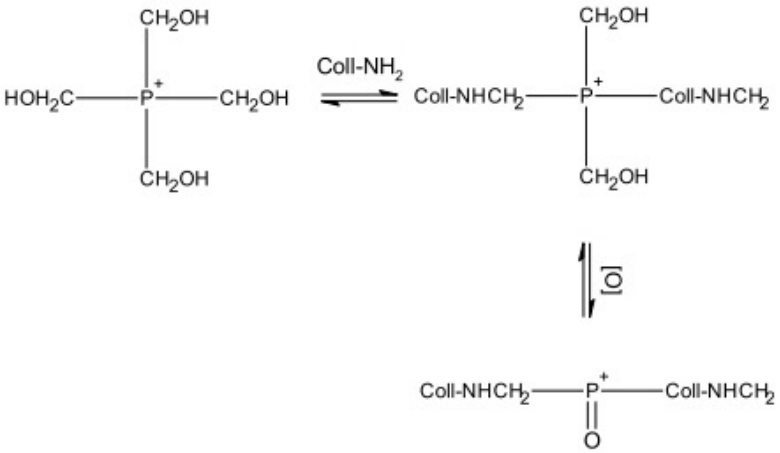

Figure 3. Reaction mechanism of phosphonium salts with collagen.

Source: Naviglio *et. al.* (2011).

According Naviglio *et. al.* (2011) as phosphonium salts react with sulfur compounds giving rise to unpleasant odors, after the use of phosphonium the hides must be treated with strong oxidizers such as hydrogen peroxide (H_2O_2) allowing greater stabilization of tanning.

Naviglio *et. al.* (2011) comments there are others mineral tanning mostly are based on aluminum (III), titanium (IV) and zirconium (IV). Using these metals hides become more cationic having problems using anionic products, by this fact requires a more accurate masking and also to prevent precipitation of metal hydroxides. But such curtimentos marketing features give the leather below the chrome tanned leather (III) with respect to softness, stuffing and retraction.

In accordance with Naviglio *et. al.* (2011), the unique approach of tanning with organic substances, either of natural origin (vegetable tannins) which synthetic origin (synthetic tannins, aldehydes, oxazolidines, phosphonium salts, paraffin sulfocloradas, etc.)

are the most modern research cutimentos alternative to chromium . It is known that vegetable tannins are known products for millennia, and synthetic tannins and aldehydes known only few decades.

3. METHODOLOGY

The methodology of this study was first to perform a mapping of the situation of the tanneries, checking its main technology needs and difficulties to minimize environmental impact.

The procedures used in this study as a basis to seek measures to minimize environmental impact, made up of combinations of traditional tanning with THPC. So were first made traditional tanning and tanning following combined.

Tests were performed with vacuns pickled hides which were dried, thus making a bath with 6º Bé for rehydration of fur. This same bath was reused in the process. To perform the 8 tests tanning pilot scale was used fulão Master of FLD-12, the chemicals were weighed in the balance of Urano UD1500/0.1 LE and the hides were weighed in the balance of brand Martin Laboratory Improvement University Feevale.

The hides were dried and downgraded the company TLC Beneficiation leather LTDA.

Each whole hide was divided into four parts according to Figure 4 which has become a meeting point for all parties to do so comparative tests between the regions closer.

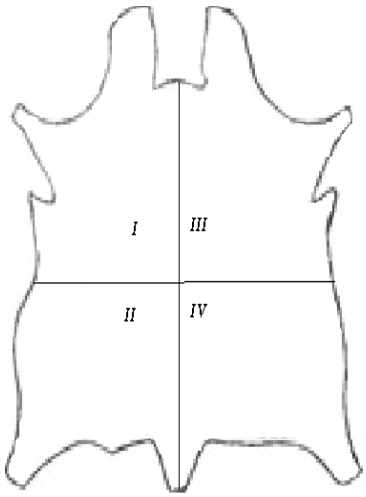

Figure 4. Division for hide testing.

The chemicals used in the formulations were donations from the companies: Noko Química LTDA, LS-Leather and Rep. Com Solution LTDA, Brazil and Chemicals MK Tanac SA, and products purchased with project funds Fapergs.

We performed a total of eight cases, which were performed by combinations of tanning.

The first hide, labeled 1 was divided into four experiments (I, II, III and IV) carried out according to table 1.

Table 1. THPC tanning combined with basic chromium sulfate.

Experimento	Curtentes
1 I	Basic chromium sulfate and sulfate Tetra-hydroxy-methyl-phosphonium
1 II	sulfate Tetra-hydroxy-methyl-phosphonium
1 III	Basic chromium sulfate
1 IV	Pretanning with Sulfate Tetra-hydroxy-methyl-phosphonium tanning and basic chromium sulfate

In table 2 we can see the formulations summarized that each part of the hide. As the pickled hides were purchased and dried was conducted the measuring the weight of each portion according to the test being carried out by adding 20 mass% wiped hide to reach the closest to the actual mass to do so tanning.

Table 2. Tanning combined THPC with modified tannin from acacia.

	1 I **SBC + THPC**	**1 II** **THPC**	**1 III** **SBC**	**1 IV** **Pretanning THPC/** **Tanning SBC**
Bath in pickling	80%	80%	80%	80%
Sodium chloride	1%	1%	_____	1%
Fatty alcohol	2%	2%	_____	2%
THPC	1%	2,5%	_____	0,5% - demote
Water	_____	_____	_____	100%
SBC	3%	_____	6%	3,5%
Sodium formate	2%	2%	_____	_____
Sodium Bicarbonate	1%	2%	2%	0,5%
Water	_____	200%	_____	_____
Hydrogen peroxide	_____	2%	_____	_____
Fungicide	0,05%	0,05%	0,05%	_____

In the second test, the hide called two, was also divided into four sections identified as shown in Table 3.

Table 1. Tanning with combined THPC with modified tannin from acacia.

Experimento	Curtentes
2 V	Acacia tannin and modified with sulphate Tetra-hydroxy-methyl-phosphonium
2 VI	sulphate Tetra-hydroxy-methyl-phosphonium
2 VII	Acacia tannin and modified
2 VIII	Pretanning with Sulfate Tetra-hydroxy-methyl-phosphonium tanning and Acacia tannin modified.

The formulations developed in experiments 2V, 2VI, 2 VII and 2 VIII are summarized in Table 4.

Table 2: Tanning combined with THPC and modified tannin from acacia.

	2 V TAM + THPC	**2 VI THPC**	**2 VII TAM**	**2 VIII Pretanning THPC/ Tanning TAM**
Bath in pickling	80%	80%	80%	80%
Sodium chloride	1%	1%	_____	1%
Fatty alcohol	2%	2%	_____	2%
THPC	1%	2,5%	_____	0,5% - demote
Water	_____	_____	_____	80%
Sodium Formate	2%	2%	2%	2%
Sodium Bicarbonate	1,5%	2%	1,5%	1,5%
TAM	30%	_____	25%	10%
Formic acid	0,5%	_____	0,5%	0,5%
water	_____	200%	_____	_____
Hydrogen peroxide	_____	2%	_____	_____

To check the environmental impact of different tanning evaluated the residual baths have been made all tests in duplicate using the following analyzes performed by the Analytical University Feevale:

- Calcium -based Standard spectrophotometry flame atomic absorption (EAAC).
- Total Chromium-based Standard EAAC;
- Biochemical Oxygen Demand - BOD5 based on Standard manometry;
- Total Suspended Solids Standard based on gravimetry;
- Chemical Oxygen Demand - COD based on Standard of titrimetric;
- Total Solids based on Standard gravimetric;
- Total Nitrogen based Standard titrimetry.

Also were analyzed and observed the leathers to assess whether the proposed changes to minimize the environmental impact caused no changes in the quality of the final product. The analyzes of the leathers were performed in two stages. First were collected after tanning operations and evaluated the following analyzes performed by the Analytical University Feevale:

- Determination of chromium oxide-based NBR 11054 2007;
- Determination of calcium content based on NBR 11030 -2012;
- Test of retraction in tanned hides, in which the hides were cut with 10x2cm and placed in boiling water for 2 min. This test was performed in the laboratory of the University Feevale processing.
- Light fastness in tanned hides: 14730:01 based on NBR -2001. This test was performed by Tanac S.A.

4. Results and Discussion

In the first tests, where there was combinations of THPC with SBC, observed in Figure 5 that better exhaustion of the bath tanning test was carried out by pre-tanning with chrome tanning and THPC, where the bath proportion to such was the only chrome tanning.

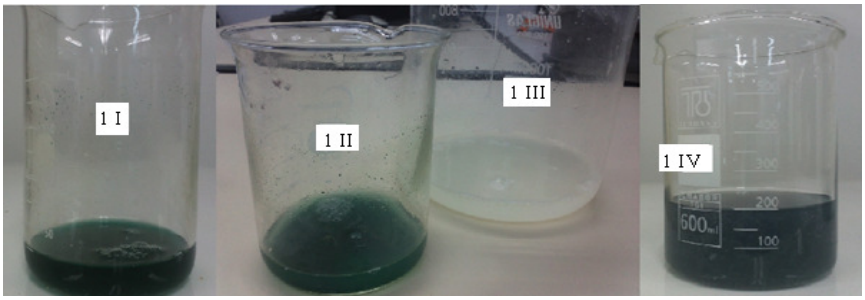

Figure 5. 1I - Tanning with SBC, 1II - Tanning with the combination of THPC with SBC, 1 III - Tanning with THPC, 1 IV - SBC tanning bath after the pretanning with THPC.

Following the same combinations were analyzed hides after tanning, the best bleaching the color, it was the combination of the SBC after the tanning pretanning with THPC, as can be seen in Figure 6. Comparing the extremes of the tanning isolated with SBC and tanning with THPC, there is a great difference in color from blue to yellow, and the two combinations, both in pretanning with THPC and in combination with THPC at SBC same bath, adds a higher bleaching of color.

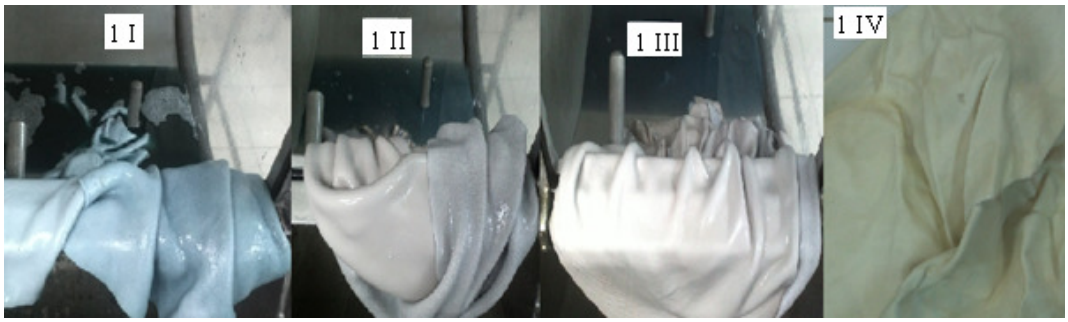

Figure 6. 1 I- Tanning with SBC, 1II - Tanning with the combination of THPC with SBC, 1 III - Tanning with THPC, 1 IV - SBC tanning bath after the pretanning with THPC.

It is shown in figure 7 the tanning bath comparative combinations of THPC with TAM. Through this, it is seen that the best combination of tests was characterized by better performance with THPC pretanning and tanning with TAM.

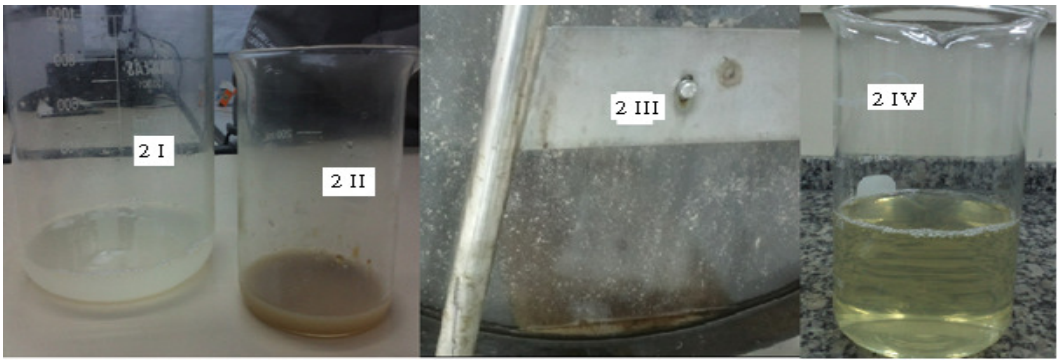

Figure 7: 2 I - tanning bath with THPC, 2 II - tanning with TAM, 2 III - tanning THPC in combination with Tam and 2 IV- tanning bath with TAM after the pretanning with THPC.

At the hides after tanning bath, it is observed in Figure 8 hides followed by combinations of TAM with THPC, which is shown as a result of better targeting the pretanning with THPC and tanning with TAM, showing the same combination of tanning in the same bathroom improved bleaching compared with the tanning only with TAM.

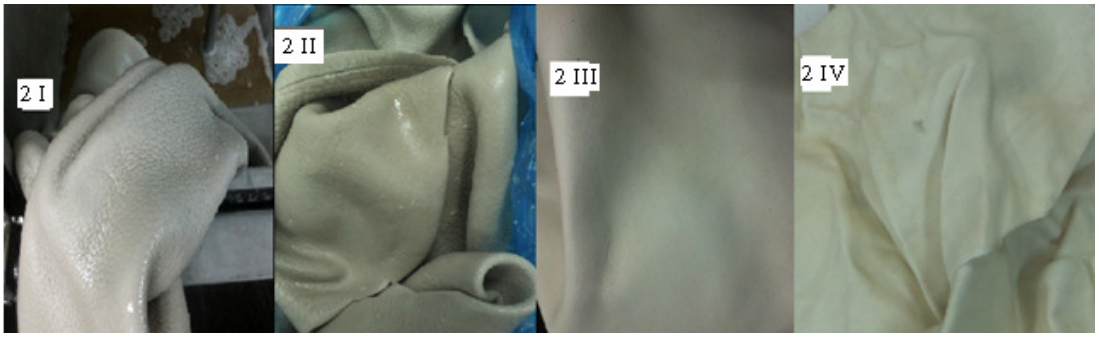

Figure 7: 2 I - tanning bath with THPC, 2 II- tanning with TAM, 2 III - tanning THPC in combination with Tam and 2 IV- tanning bath with TAM after the pretanning with THPC.

The tanning only with THPC was held in one of the parts of the hide that held the combinations with chrome and tannin order to compare the tests performed on the same raw material.

As one of the goals of using THPC is targeting the clarified, the acacia modified tannin used in the process is tannin modified and clarified.

As the goals of decreasing demand of waste generated, as can be seen bathing in the visual aspects, it is observed that there existed a large depletion when combined with THPC, mainly in use as pre-tanning.

It is analyzed that with respect to the basic chromium sulfate tanning in the tanning and combining SBC with the second tanning THPC was more absorption of tanning the hide in comparison to exhaust the bath tanning.

The pre-tanned hides were wiped dry with THPC and after lowered and returned to drum to the tanning process, it was observed that both the chrome tanning as to TAM, there was great and rapid exhaustion bath crossing tanning of the hide.

All leathers were downgraded in thickness 12/14mm, and received only the hides split, in which it took place pre-tanning, tumbler, themselves before tanning, and the others were demoted after tanning. Only one equalization, the hides that are pre-tanned leather after tanning were lowered again in the same sized to a uniform thickness.

According to the resolution Consema No. 128/2006, legislation used in the state of Rio Grande do Sul, for the flow of 20 m^3/do emission ceiling for BOD5 is 180mgO_2L^{-1} and this value for COD is 400 mgO_2 / L. It is observed in table 5 in that refers to BOD_5 tests 1II, 2V and above 2VII were waiting, but the other tests, all followed within the parameter of resolution. As regards the COD none of the tests passed the parameter resolution, so when analyzing smaller amounts of COD BOD_5 combined with the best combination would be the tanning pretanning and tanning with THPC with SBC, with best results in tanning only chromium.

Table 5: BOD5 and COD of wastewater from baths distinct tannings.

Tanning / Combinations	Identification	BOD em mgO_2/L	COD mgO_2/L
SBC e THPC	1I	100	6167,7
THPC	1II	65	16694
Washing with hydrogen peroxide	1 II (H_2O_2)	260	8083,3
SBC		5	3562,6
Pre tanning with THPC	1IV (a)	30	7782,4
Pre tanning with THPC and tanning SBC	1 IV (b)	40	4959
TAM e THPC	2 V	600	16626,1
THPC	2 VI	65	16694
TAM	2VII	800	60670,8
Pre tanning with THPC and tanning TAM	2 VIII (a)	30	7782,4

The result of high concentrations for tests with tannins was expected, since the main waste generated in step tanning with vegetable tannins it is the waste liquid containing a high content of tannins, polyphenols, which by their high molecular weight and volume presents much organic load in the bath. Furthermore, the high organic load in the waste liquid requires high oxygen consumption (MOREIRA E TEIXEIRA, 2003).

But as stated earlier, tanning on the combination of TAM with THPC had great improvement in the low sediments at the bath , so we can say that the process was optimized. According Moreira e Teixeira (2003), one can use the application of an efficient recycling of the residual vegetable tanning baths reducing considerably the toxic load of the tannins in the effluent. With respect to test 2 VIII (b) could not parse because there were analytical problems.

In Table 6, it is observed in the analyzes that are without result of solids, is the fact the bath be greatly reduced there was sufficient for this analysis, so it was not possible in all cases to compare the total suspended solids. Taking into account that by being short baths, values of total solids and suspended solids were high. It should be noted that in these tanneries waste baths are treated before disposal.

Table 6: Total solids and total suspended solids of the various baths residual tannings.

Tanning / Combinations	Identification	Total Solids	Suspended Solids
SBC e THPC	1I	59500	1113,8
THPC	1II	--------	90433
Washing with hydrogen peroxide	1 II (H2O2)	396	36200
SBC		602	63263
Pre tanning with THPC	1IV (a)	1640	168758
Pre tanning with THPC and tanning SBC	1 IV (b)	1640	22762
TAM e THPC	2 V	87278	4762
THPC	2 VI	--------	90433
TAM	2VII	2210	97545
Pre tanning with THPC and tanning TAM	2 VIII (a)	1640	168758

Aquim (2004), in their tests of conventional washing after liming was found 1450 mg / L of calcium using these values as parameters, it can be seen in Table 7 that the best results were tanning test SBC and THPC, followed test pre-THPC tanning and tanned with SBC, the others were all above the traditional tanning, which shows that perhaps the deliming process has not been effective, but the results would be good because the process has improved this aspect analyzed in the bath. The calcium values in the residual bath, depend on the operations of beamhouse, since the process for deliming objective remove calcium from the skin. However when not performed successfully calcium remains in the following steps.

Table 7. Calcium concentration of residual baths of different tannings.

Tanning / Combinations	Identification	Calcio mg/L
SBC e THPC	1I	29,904
THPC	1II	31749,9
Washing with hydrogen peroxide	1 II (H2O2)	11788,6
SBC	1 III	13495,1
Pre tanning with THPC	1IV (a)	30389,5
Pre tanning with THPC and tanning SBC	1 IV (b)	6347,1
TAM e THPC	2 V	196,844
THPC	2 VI	31749,9
TAM	2VII	12839,5
Pre tanning with THPC and tanning TAM	2 VIII (a)	30389,5

According to CONSEMA 128/2006, with regard to oils and greases, the value must be less than 30 mg / L, the amount of total nitrogen with a flow rate between 100 and 100 m3 / d is 20 mg NTKL / L, and the amount of total chromium is 0.5 mg Cr/ L.

By analyzing the table 8, the concentrations of Total Nitrogen, it is observed that the only test that has resulted within the parameter was the combination of THPC with SBC in tanning, the other tests were all with above results. With regard to the results of oils and greases, it is observed that only result is within the parameters tanning with SBC, noting that the results of baths containing TAM always have greater values organic load.

According Moreira (1994), tanning baths residual quantities of Cr_2O_3 is 6000 mg / L to 8000 mg / L. It is observed in the results shown in Table 8, that all baths were left with lower values, demonstrating the optimization of the process, noting that the lowest value was the combination of pre-THPC tanning and tanning with SBC in getting 301.275 mg / L. As Aquim (2009), In their experiment pilot tanning with SBC resulted in a residual bath with 2030 mg / L, quite close to the result obtained in the first experiment III (tanning only SBC) which was 2152.8 mg / L, and combining the two tanning in the same bath (test 1 I), was 394.62 mg / L. It is observed thereby that the combinations with THPC significantly decreased the concentration of Cr2O3 in the baths, the best alternative in the pretanning with THPC and tanning with SBC.

Table 8: Concentration of total nitrogen (Kjeldahl), Oil and Grease and Total Chromium baths residual tanning distinct.

Tanning / Combinations	Identification	Total Nitrogen mg/L	Oil and Grease mg/L	Total Chromium mg/L
SBC e THPC	1I	10,19	127,3	394,62
THPC	1II	185,81	334,6	3,903
Washing with hydrogen peroxide	1 II (H2O2)	115,25	110,6	0
SBC		156,8	8,1	2152,8
Pre tanning with THPC	1IV (a)	150,53	123,5	0
Pre tanning with THPC and tanning SBC	1 IV (b)	279,41	146,5	301,275
TAM e THPC	2 V	688,35	499	0
THPC	2 VI	185,81	334,6	0
TAM	2VII	526,85	203,6	0
Pre tanning with THPC and tanning TAM	2 VIII (a)	150,53	123,5	0

The results of the chemical tests performed with the leathers under study can be checked in Table 9. These analyzes show chrome oxide and calcium made ourselves after the tanning processes.

Table 9. Analysis of chromium oxide, calcium and extractable in dichloromethane of the different tanning leathers.

Tanning/Combinations	Indentification	Chrome Oxide (dry basis) % Cr_2O_3	Calcium (dry basis) %
SBC e THPC	1I	1,49	0,03
THPC	1II	------	0,02
SBC	III	2,29	0,04
Pre tanning with THPC and tanning SBC	1 IV (b)	0,2	0,04
TAM e THPC	2 V	------	0,07
THPC	2 VI	------	0,02
TAM	2VII	------	0,07
Pre tanning with THPC and tanning TAM	2 VIII	------	0,07

According to Table 9, we observe that all results of C_r2O_3 were below what is required by the standard which defines the requirements of a wet-blue leather, NBR 13525:1995, which is 3.5% Cr_2O_3, expected a better result in the first test to be a tanning III with 6% of SBC, however fulão pilot was made in less than industrial mechanical action, since the other tests were not only tanned with chrome, accepting these results as well.In accordance with

Borba, Peres e Webwe (1993), accept the maximum amount of calcium is 0.3%, concluding that all outcomes are below.

Was realized tests were retraction of leathers only with tanning , as noted in the figure 8 with leather where had combinations with SBC,and in Figure 9 tests with the combinations the TAM. Table 8 shows the shrinkage test results in the tanned leather. According Naviglio *et. al.* (2011), the leathers tanned with THPC in temperature of 100 ºC, the reduction is around 25%, showing great bleaching, light fastness and perspiration. With that sought to improve such characteristics in the proposed combinations.

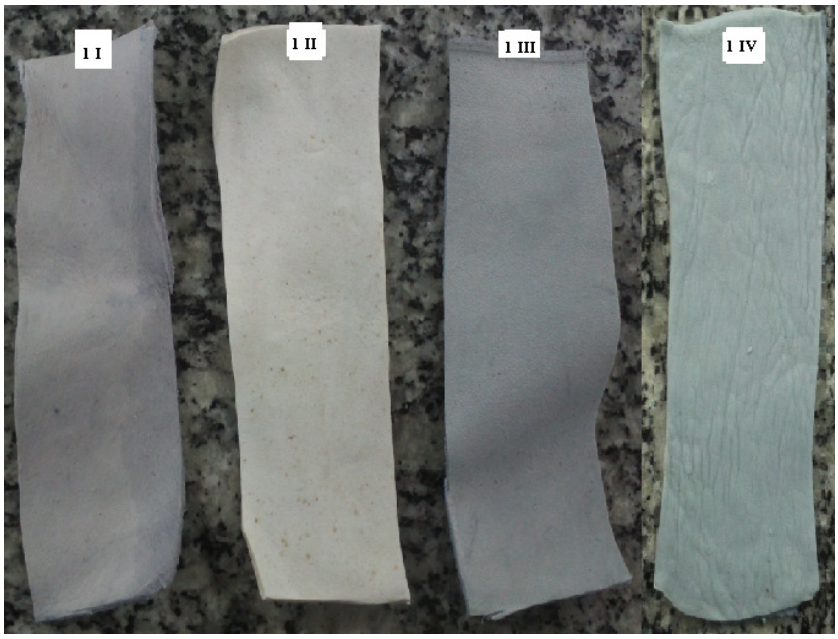

Figure 8. 1 I - tanning with the combination of THPS with SBC, 1 II - tanning with THPS, 1 III - IV tanning with SBC and 1 IV- tanning SBC pre-tanned with THPC.

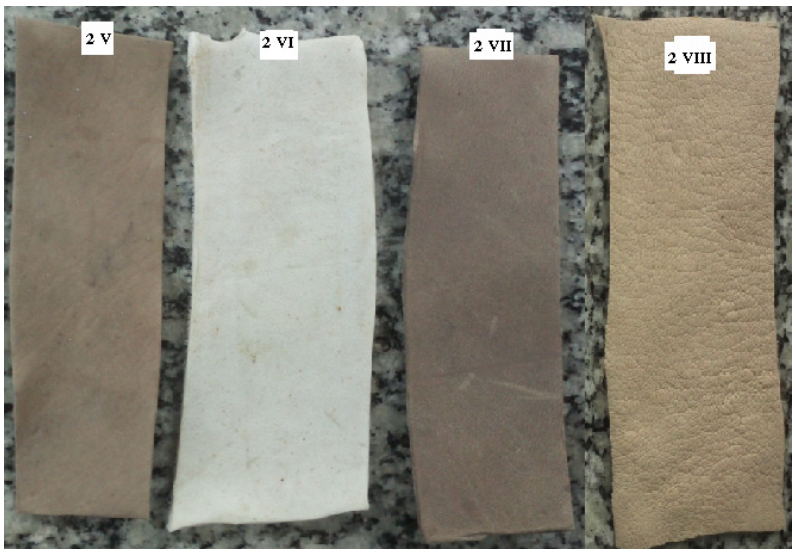

Figure 9. 2V - tanning with the combination of THPS with TAM; 2 VI - tanning with THPS; 2 VII - tanning with TAM and 2 VIII - tanning with TAM with the pre-tanned leather with THPC.

In Figures 10 and 11 there are the testing results of the light fastness performed on only tanned leathers in order to have a comparison with use of only tanning product without any interference on the result.

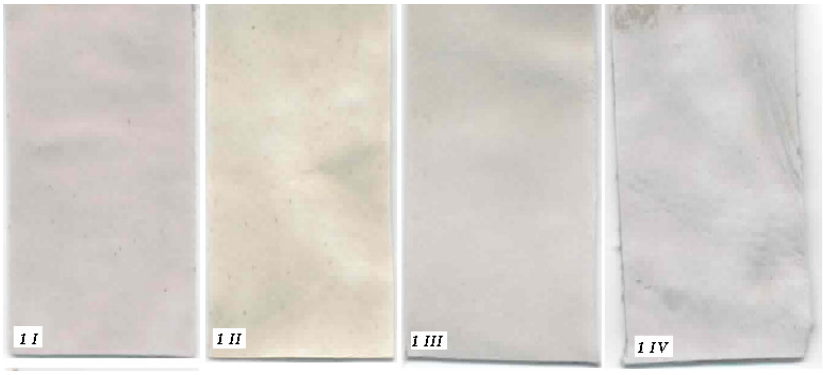

Figure 10: Strength in light tanned leathers with combinations: 1 I - tanning coma THPS combination with SBC; 1 II - tanning with THPS; 1 III - tanning with SBC and 1 IV - tanning with SBC in pre-tanned with THPC.

According to figure 10, we can observe the light fastness test performed in leathers tanned with only combinations of SBC with THPC, while the part which has been exposed to light the top of the samples. In Tanac SA where tests were conducted, the results are not evaluated the samples with scales blue or gray, is made only comparative test of all. According to the test results the best combination of tanning with respect to the light fastness was the pretanning with THPC and tanning with SBC, with no difference in the light exposed portion and the portion covered since the combination of both tannins in tanning, there is a slight reddening in the sample.

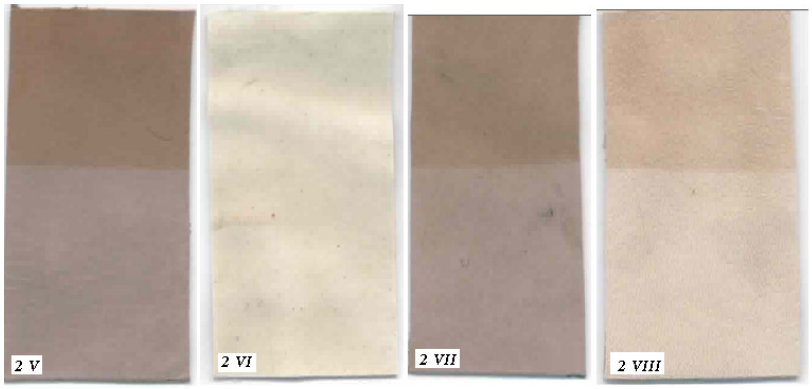

Figure 11: Test for fastness to light with combinations: 2V - tanning the combination of THPS with TAM; 2VI - tanning with THPS; 2VII - tanning with Tamoxifen and 2 VIII - pre tanning with THPC and tanning with TAM.

The test shown in Figure 11 follows the same test procedures of Figure 10. What can be noted is that the use of THPC in the same bath tanning TAM did not have much effect with regard to tanning with TAM alone, but it is clear improvement in both light fastness, as the improvement in color combining the pretanning and tanning with THPC an tanning with TAM, where there bleaching the color of the leather.

4. Conclusion

As a very worrying factor in the leather industry pollution load to be discarded in the form of liquid or solid waste this study achieved its objective, since it was possible, through new proposals tanning, decrease the amount of harmful to the environment, bringing alternative combinations that were efficient in tests.

It was concluded with all tests using the THPC was a good bleaching brought to hides, tanning both in comparison with the SBC and the combination thereof with THPC, as compared with the tanning combination with TAM and THPC, and in both tanning combined with THPC, the tanning we got the best result was targeting the combination of pre-THPC tanning and with TAM and SBC.

As noted in the analysis of residual baths and during the process, comparing all pilot tests carried out, the suggestion of pre tanning with THPC and tanning with both SBC or with TAM, the best results were exhausted baths.

In all the results shown in work, it was observed that with respect to the SBC the best result was obtained with the combination of THPC in tanning. In combination with TAM, the best result was obtained in combination with the pre-tanning THPC and tanningTAM.

By all the results obtained, it was found that there was good results in the final product, leather, helping to minimize the environmental impact of waste with decreasing pollutants.

5. List Of Abbreviations And Acronyms

SBC	Basic Chromium Sulphate of
THPC	Sulfate Tetra-hydroxy-methyl-phosphonium
THPO	Tri-hydroxymethyl-phosphine
TAM	Acacia tannin Modified
NBR	Brazilian Standard
REACH	Registration, Evalutation, Authorization and Registration of Chemicals European Chemicals Agency
COD	Chemical Oxygen Demand
BOD_5	Biochemical Oxygen Demand
pH	Potential of Hydrogen
EAAC	Atomic Absorption Spectrometry Flame

6. Acknowledgements

- Fapergs
- Universyity Feevale
- Tanac S.A.
- LS-Leather Solutions Comercio e Representações LTDA

7. References

ADZET, J. M.;MASSANELA, G.E; ESCUDERO, R.L.; *et al.*. **Quimica Técnica de Teneria.** Barcelona: Bosch, 1985.

AQUIM, P, M.. **Gestão em Curtumes: uso integrado e eficiente da água.** Universidade Federal do Rio Grande do Sul, Escola de Engenharia. Programa de Pós-Graduação em Engenharia Química. Tese de Doutorado, 2009.

_____. **Balanço de massa:** uma ferramenta para otimizar os processos de ribeira e curtimento. Universidade Federal do Rio Grande do Sul. Escola de Engenharia. Programa de Pós-Graduação em Engenharia Química. Tese de mestrado, 2004

ASSOCIAÇÃO BRASILEIRA DE NORMAS TECNICAS. **NBR 11054:** informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, janeiro 2008.

_____. **NBR 11030**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, agosto 2012.

_____. **NBR 11030**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, agosto 2012.

_____. **NBR 14730**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, setembro 2001

_____. **NBR 11669**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, junho 2006.

_____. **NBR 11055**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, outubro 2005

_____. **NBR 12840**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, junho 1993.

_____. **NBR 12845**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, outubro 2005

_____. **NBR 12830**: informação e documentação: publicação periódica científica impressa: apresentação. Rio de Janeiro, abril 2005.

BASF, **Vade-mécum do Curtidor**, 5º edição revisada e ampliada, 2005.

BORBA, A.L.; PERES, R.M.; WEBWE, J.C. **Padronização de *wet-blue* – Uma nova etapa no Processo de Curtimento.** XXII Congresso IULTS. Brasil, Anais vol. I, 1993.

DRAULT, N., Ing.. **Anáis Del Ciclo de Vida de uma curtiembre**. XVI Congresso FLAQTIC. Pag. 105-178. Buenos Aires 6-8 Outubro, 2004.

_____. **Analisis de ciclo de vida en uma curtiembre**. XVI Congresso Latinoamericanode Químicos e Técnicos da Industria do Couro, Buenos Aires, 2004. *Anais em cd room.*

FINK, G., - LANXESS. **Formaldeído livre no couro**, Revista do Couro, n. 191, p.72 – 80, 2007.

FUCK, W. F.. **The influence of Chromium supplied by tanning and wet finishing processes on the formation of Cr(VI) in leather.** Federal University of Rio Grande do Sul, Chemical Engineering Department, Laboratory for Leather and Environmental Studies, (LACOURO), 2011.

_____. **Influência do teor de cromo e do tipo de óleo na formação de cromo hexavalente no couro.** Universidade Federal do Rio Grande do Sul. Escola de Engenharia. Programa de Pós-Graduação em Engenharia Química (Dissertação de Mestrado). 2008.

GUSTAVSON, K.H. **The Chemistry of Tanning Process**. Academic Press INC, 1956.

GUTTERRES, M., SANTOS, L. M.. **Reusing of a Hide Waste for Leather Fatliquoring**. Journal of Cleaner Production, v. 15, p. 12-16, 2006.

HOINACKI, E.; MOREIRA, Marina. Vergilio.; KIEFER, Carlos. Guilherme. **Manual básico de processamento do couro**. Porto Alegre: SENAI/CTC, 1994.

HOINACKI, E.. **Peles e couros: Origens, defeitos e industrialização**. 2ª ed. Porto Alegre. 1989.

LAMB, L.H.; SARMENTO, L. I. N., HASS, M. E. A., *et al*..**Extratos de Mimosa modificados quimicamente para obter-se melhor solidez a luz.** XVII Congresso ABQTIC, Anai vol. 1, 2005.

MOREIRA, M. V,; TEIXEIRA, R. C.. **Estado da arte tecnológico em processamento do couro: revisão bibliográfica no âmbito internacional**. Porto Alegre: Centro Nacional de Tecnologias Limpas (Projeto Desenvolvimento Sustentável da Indústria do Couro em MG e no RS), 2003.

MOREIRA, M. V.In: HOINACKI, E., MOREIRA, M. V., KIEFER, C. G. **Manual Básico de Processamento do Couro**. SENAI/RS, Porto Alegre. 1994.

NAVIGLIO, B., *et. al.* **Sistemas de curtimentos alternativos ao cromo, Chrome Free e Metal Free.** Departamento dos estudos, das instituições e dos sistemas territoriais, universidade dos estudos de Nápoles "Pathenólpe", 2011.

NISHAD, F. N., ARAVINDHAN, R., RAGHAVA, RAO J., Balachandran, N. U.. **Tannic Acid-Phosphonium Combination:** A Versatile Chrome-Free Organic Tanning. Journal of the American Leather Chemists Association, 101, 161 – 168, 2006.

NISHAD, F. N., RAGHAVA, R. J., BALACHANDRAN, N. U.. **Studies on Phosphonium Based Combination Tanning:** Less Chrome Approach. Journal of the American Leather Chemists Association, 106, 249 – 256, 2011.

PACHECO, J. W. F. **Curtumes.** São Paulo : CETESB, 2005. Disponivel em <http://www.cetesb.sp.gov.br> acesso em Agosto 2012

PAIVA, R. M. M.. **Aplicação de cálculos químicos no estudo de espécies de cromo relacionadas ao processo de curtimento de peles** . Dissertação de Mestrado em Tecnologia de Materiais e Processos Industriais da Universidade Feevale, 2011

PASSOS, J. B.. **Reuso de água: uma proposta de redução do consumo de água em curtumes.** Universidade Federal do Rio Grande do Sul. Escola de Engenharia. Programa de Pós-Graduação em Engenharia Química (Dissertação de Mestrado). 2007.

RAJAMANI, S.; STREIT, K. F.;, CASEY P.. **Environmental update on world leather sector from International Union of Environment (iue) Commission of IULTCS.** In: XVIII Congresso Latino-Americano dos Químicos e Técnicos da Indústria do Couro, 2008, Rio de Janeiro. Anais do Congresso da FLAQTIC, 2008.

REINEKING, C., WALKER, M., MA., S. – CLARIANT INTERNATIONAL, **Formaldeído em couro – ocorrências e soluções**, anais ABQTIC 2005.

RODRIGUES, F.D.R. Amado, J.L.N. Xavier, K.F. Streit, A.M. Bernardes, J.Z. Ferreira **Application of photoelectrochemical–electrodialysis treatment for the recovery and reuse of water from tannery effluents** Journal of Cleaner Production, Volume 16, Issue 5, P. 605-611. Março, 2008.

SAMMARCO, U., **Processo inovador d e curtimento com excelente esgotamento.** Revista do Couro, n. 186, p. 112 – 116, 2006.

_____. **Aspectos tecnológicos, ambientais e toxicológicos no moderno trabalho do couro**, Revista Internacional Tannery, n. 183, p. 51 – 68, 2004.

SCAPINI, L.. **Avaliação do desempenho da osmose reversa e da troca iônica para tratamento de efluente de curtume (Aimoré Couros Ltda – encantado) visando a reutilização da água**. Dissertação apresentada ao Programa de Pós-Graduação Sistemas e Processos Industriais – Mestrado, Área de Concentração em Instrumentação, Sistemas de Medição e Tratamento de Dados, Universidade de Santa Cruz do Sul, 2007.

SILVA, R. C. **Influência da massa molar e estrutura de polímeros acrílicos monodispersos como recurtentes em couros**. Dissertação de Mestrado da Universidade Federal do rio Grande do Sul, 2007.

SREERAM, K. J; RAMASAMI, T.. **Sustaining tanning process through conservation, recovery and better utilization of chromium**, Resources Conservation & Recycling, 38, 185 – 212, 2003.

STREIT,K. F.; Xavier a , J. L .N.; GONDRAN , E.; RODRIGUES, M. A. S.; BERNARDES, A. M.; FERREIRA ,J. Z.. **Reciclagem de água de processos de curtimento.** Disponível em http://www.aaqtic.org.ar/congresos/brasil2005/pdf/Reciclagem.pdf. Acesso em Agosto de 2012

WENZEL, B. M.; MARCÍLIO Nilson Romeu. **Redução carbotérmica do cromo contido nas cinzas do tratamento térmico de resíduos de couro visando a obtenção de liga ferrocromo e sulfato de cromo.** Universidade Federal do Rio Grande do Sul, UFRGS, Dissertacao de Mestrado, 2008 .

WOLF, G., Hüffer, S., FRECH, P., - (BASF AG), **Formaldeído no couro:** causas e como evitar**,** Revista do Couro, n. 155, p. 58 – 65, 2002.