

Italian high technology of TANNING



Guideline n°1 - 2nd

BEAMHOUSE

Guidelines for a more sustainable tanning processes; are designed for consider the specific issues and addressing dedicated suggestion or possible operational solutions to a better control of resources and contribute in limitation of the environmental impact of the process.



Published in 2007 A.T.O. Valle del Chiampo A.A.T.O. Bacchiglione

Guidelines published in 2007. This work was the result of the impact assessment of tanning process in the Arzignano district, specifically drawn to indicate the need for a better control of wastewater entering in the treatment plant and meet parameters in the output according to the Italian Regulation. A special thanks is due to Mr. Hans George Hoerter, Dr. Raoul Sartori and the late Dr. Umberto Sammarco for their availability in the drafting of the Guidelines **by courtesy of Acque del Chiampo SPA**

Translation and Reprint by ASSOMAC SERVIZI S.r.l.



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1. GUIDELINES FOR THE CHLORIDE REDUCTION in Tannery wastewater

Sodium chloride is mainly used in the tanning process preservation of raw hides and during pickling to suppress the acid swelling. The environmental impact of chlorides, respect to the two phases mentioned above, has a different incidence.

1.1. CHLORIDE from CONSERVATION of RAW HIDES

The amount of salt needed to ensure a long-term safe storage amounts to about 30% by weight of raw hides. It is estimated that over 70% of chlorides present in wastewater of the entire production process comes from salt used for leather conservation.

The methods of treatment for this pollutant are very expensive even for high investments and for the requested high energy contribution. At this time the replacement of salt with other products and/or alternative non-polluting methods is still not yet feasible at large scale, therefore the reduction of sodium chloride used when salting can be done by implementing the following *Best Available Techniques*.

1.1.1. Raw hides beating

The salt quantity that can be eliminated through this approach is related to the raw hides provenience and approximately can be calculated on the weight of raw hides. The amount of salt removed by this operation varies depending on the origin of the raw between 6 and 12% calculated on the weight of the raw hide. To increase the efficiency of the operation it is recommended to increase the beating time and decrease the inclination of the drum. A system for verifying the effectiveness of beating is to run an occasional re-whisking of lower rates of skins. The weight difference found between the first and second the operation should not exceed 1%.

1.1.2. Using fresh raw hides

The contribution in reduction of chlorides into waste water processing fresh raw hides is evaluated at least 40%. In a mixed production (50% and 50% of freshly salty) you can get a reduction of over 20%. Many European countries use fresh skin for a long time in significant quantities.

On the other hand, for the processing of fresh hides must be taken into consideration a few things:

- Italian tanneries may have fresh supplies of hides only from Europe;
- Substantial supplies are not in case of substantial price fluctuations.



- The skin should be kept at a temperature of 2° C during transport and storage in the tannery;
- Storage can not be continued for longer than 7-8 days;
- The need to keep your skin at low temperatures is really expensive related to the energy consumption.

The limitations related to the process of fresh raw hides may be muffled with a rigorous organization. Beyond the limits listed above first, however, be solved with proper business organization, processing of hides presents fresh following advantages:

- the stock does not present fairly common defects due to salting (spots, damage the grain);
- o the authenticity of origin can be identified more easily;
- the elimination of row hides beating and manage of the salt waste.

1.2. CHLORIDE REDUCTION IN PICKEL

The bath density, compared with common average in use (8-9 °Bé), can be reduced significantly anyway avoiding the acid swelling. A density of 6.0-6.5 °Bé ensures proper execution of this operation. This parameter will be checked each time, after a rotation of 20 minutes by the addition of salt. To further reduce the amount of salt it is necessary to work in a fairly short float. The 20-35% on the pelt weight (depending on whether you use liquid chrome or powder) is more than enough, since the substantial increase in volume resulting from the addition of diluted acid. For safe operation it is advisable to recheck the density even after the addition of acids.

It must not be less than 5.5 °Bé, this value still guarantees maximum operational safety. Moreover, it is known that non high density values produce a better quality leather.

Another benefit from the short float is an increased speed of the acids in crossing of the leather section, resulting in time savings that can be conveniently used in the later stage of tanning. These measures allow a drastic reduction of the salt used in pickling (30%), which can be quantified in a decrease of about 10% of the total chloride discharge ¹.

 $^{^1}$ Calculated assuming the use for each kilogram of raw skin of 25 liters of water for a complete processing cycle, an average content of 3000 mg/l of sulfates of 7000 mg/l of chloride and 200 mg/l Cr in the effluent at the end of the process.



2. GUIDELINES FOR THE SULPHATES REDUCTION in Tannery wastewater

The predominant amount of sulphates present in wastewater comes from the deliming, pickling, tanning phases as well as from sulfur present in the effluent at the end of liming, which turns into sulphates during depuration phases. Less significant contributions of sulphate, especially when the complete cycle is carried out, are due to the dyes and retanning used.

2.1. REDUCTION OF SULPHATES ORIGINATED FROM OXIDATION OF SULPHITE

It is known that sulfide from wastewater by liming may be oxidized to sulphate during water purification. Assuming that oxidation is complete, the reduction of 1% of the sulfur offer in liming phase would determine a reduction of sulphate in wastewater of about 300 mg/l¹.

The main systems, which allow the reduction of the sulfur supply, are based on the following measures:

- Simultaneous use of assisting substances. They enable an efficient hair removal using a total amount of sulfur and hydrogen sulphate equal to 2-2.5%;
- Reintroduction of the hair recovery. This technique allows a liming with a total offer of sulfur and hydrogen sulphate equivalent to 1.5-2.0% compared to the traditional 3.0-3.5% used for liming with hair destruction. Swelling and turgescence can be adjusted by adding dilute caustic soda. The hair recovery also helps the not inconsiderable advantage of a load reduction of COD, TKN and suspended solids;



Recovery and reuse of the bath at the end of liming appropriately reintegrated with lime and sulfur. Obviously, in this case the emissions of sulfur and consequently of sulphate will be reduced to a minimum. This system saves a vital resource like water and about 20% of sulfur and lime. Spending on plant recovery could be depreciated quickly enough due to less consumption of agents liming. The lower use of sulfur allows a reduction of the reagents used for the abatement of emissions during the deliming and pickel phases.

2.2. REDUCTION OF SULPHATES IN DELIMING

At this stage sulphates come from ammonium sulfate, which is the most widely used deliming for reasons of price, better speed cross section and for his buffering effect. Really, the pH of the bath never drops below the safety threshold when this product is used as deliming agent. Unfortunately, it also helps to raise the effluent TKN values. On the other hand, the deliming of full thickness heavy hides using products free of ammonium salts is hardly feasible, as the lead times of the process would be too long.

It's realistic, and industrially feasible, the partial replacement of this salt, at least 50%, with products based on alternative mixtures of dicarboxylic acids and / or organic esters.

This measure would lead to a reduction of over 10% of sulphates present in the effluent in the entire processing cycle.

It should be stressed that the new generation deliming allows to make a full thickness skin deliming with a supply of ammonium sulphate of about 0.5% versus 2.5% medium used. This means to reduce the contribution of sulphates in the effluent of 580 mg / I, a value corresponding to about 20% of total ¹. The use of these products also offers the advantage of obtaining better items in quality compared to those obtained by making deliming with ammonium sulfate used alone.

2.3. REDUCTION OF SULPHATES IN PICKEL

Unfortunately there isn't now a viable alternative for replacing sulfuric acid during pickling. On the other hand, the contribution of sulfate due to the use of this acid has been estimated about 500 mg / l in wastewater, ¹.

The use of precise instruments (pH meters) to control the degree of acidity of the pickling solution avoids an excessive unwanted use of sulfuric acid.

Even a very well done deliming and a washing very efficient at the end of maceration allow the attainment of pH desired end pickel with and the cross section of the skin, without unnecessary waste of sulfuric acid.

¹ Calculated assuming the use for each kilogram of raw skin of 25 liters of water for a complete processing cycle, an average content of 3000 mg/l of sulfates of 7000 mg/l of chloride and 200 mg/l Cr in the effluent at the end of the process

2.4. REDUCTION OF SULPHATES IN TANNING

The improvement of the chrome exhaustion in the tanning allows the reduction of supply. This eventuality offers a considerable economic advantage. By reducing the supply of chrome, respectively 1% as powder or 2% as liquid (13%), the contribution of sulphates in wastewater is reduced to about 200 mg/l, which represents a decrease of over 6% of the total amount of sulphate in the effluent end of pipe.

In fact, it's known that every kilogram of chrome powder (25% of Cr_2O_3) contains 540 g of basic chromium sulphate and at least 300 g of sodium sulphate, corresponding to 314 g and 203 g of sulphate ion. This means that reducing the supply of chromium by 1% of chromium a total decrease of 517 g of sulphate is obtained, equivalent to about 200 mg/l of sulphate in the effluent of the complete working cycle ¹.

2.5. REDUCTION OF SULPHATES FROM DYES and RETANNING AGENTS

It's not possible to quantify, in a reliable way, the contribution of sulphates of the dyes and retanning agents used during post-tanning, because the applied formulations change within wide limits depending on the tannery and the final product. Generally dyes can contain sodium sulphate (Na_2SO_4) and sodium chloride (NaCl) in quantities between 10 and 30%, although in certain cases higher levels have been found. Assuming to use a dye containing 30% by weight of sulphate and dosing that in 4% on the weight of shaved cattle hides to mm. 1.2/1.4, the amount of sulphate in wastewater would amount to a total of about 100 mg/l_{1,2}.

Some products used in re-tanning such as resins, synthetic tannins, re-tannings and dispersants often contain significant amounts of sulphate. It's therefore preferable to use high concentration products and therefore with a low content of sulphates and chlorides.

 $^{\rm 2}$ Calculated considering the dyeing of 1 kg of wet-blue, shaved 1.3/1.4 mm. corresponding to 4 kg. raw hides

¹ Calculated assuming the use for each kilogram of raw skin of 25 liters of water for a complete processing cycle, an average content of 3000 mg/l of sulfates of 7000 mg/l of chloride and 200 mg/l Cr in the effluent at the end of the process.





3.GUIDELINES FOR THE TANNING CHROME REDUCTION in Tannery wastewater

The reduction of chrome in water at the end of tanning may be primarily done in 2 ways:

- chrome recovery by precipitation with alkali and redissolution in sulfuric acid. Chrome regenerated with new fresh tanning agent is used in the subsequent chrome tanning phase.
- optimization of the efficiency of chrome fixation to leather and exhaustion of the tanning baths.

3.1. CHROME RECOVERY

This system has some limits:

- wastewater spill of significant quantities of chromium, physically not cross-linked into the skin;
- the need to have a recovery plant;
- the not economically advantageous applicability for small and medium-sized productions;
- the need to carry out continuous analytical monitorings of chrome obtained;
- the inapplicability in the production of certain types of articles of high quality range. The first point limits ecological performances of this method. In fact, we must point out that using this system, at the end of tanning chrome not chemically bound is contained in the skin.

The amount of chromium adsorbed at a physical level is proportional to the concentration of tanning agent left in the bath at the end of tanning.

The highest the concentration is, the highest the amount of spilled chrome is in waste water through the setting out operation after washing and shaving.

While the squeezing bath may be sent to the recovery of chrome, the same can not be implemented, for obvious reasons, with the washing baths for large volumes to process. Therefore, significant amounts of chrome escape from recovery founding in wastewater and then in sewage sludge.

Moreover, recovery would result an economically disadvantageous operation and difficult to carry out for end tanning baths with a limited concentration of chrome.

3.2. OPTIMIZATION OF THE CHROME FIXATION

The improvement, within certain limits, of fixation and exhaustion of chrome, is the system of more easily applicable reduction of chrome in wastewater.

Unlike the methods with a too forced exhaustion, the systems that are based on this concept, do not interfere with the quality of some high level items.

The optimization of the chrome fixation does not require additional equipment and can be obtained without being different from the normal processing methods. In addition, the articles produced have a quality comparable to that obtained with the standard methods for chrome tanning.

Any tanning optimization system must ensure to leather the same amount of Cr2O3 of the standard working, ranging from a minimum of 3.5 to a maximum of 4.2% (at 0% of humidity) and a shrinkage temperature above 100 °C.

The main parameters that influence the efficiency of fixation are as follows:

Amount of chromium salt (in Cr₂O₃)

A smaller amount of chrome is adequate if upholstery leather are produced, while the higher one is required when leather for shoes is made.

The use of excessive amounts of chromium is not recommended, since it would only increase the concentration of tanning agents and of suspended solids in water discharged.

At the same time the quality of the article is not improved, while the costs of production increase and sometimes the mechanical strength of the skin gets worse.

Float, long

The efficiency of the pickel bath changes depending on the fact that chrome is liquid, or in powder, because during tanning process it's necessary to have more or less the same volume of bath. In the first case, the pickel is made with 20-25% water, in the second case with 30-35%. The short float ensures a faster penetration of chrome, a rapid rise in temperature, which allows to take advantage of the thermal effect for a longer period of time.

Final temperature of tanning



This parameter is very important for the performance of fixation. It's obvious that a final temperature of 40°C ensures a good return on fixation without modifying the characteristics of grain and mechanical strength.

Duration of tanning

The fixed quantity of chrome increases according to the duration of the process. It is therefore recommended, as an indication, that the duration is not less than 10 hours from the time of chrome addition.

pH of the end tanning

The pH of the end tanning should be between 3.8 and 4.0 for upholstery leather. For footwear articles it's recommended not to exceed a value of 3.9. The size of pH should be made by reliable and accurate instruments. To have a pH value of the end tanning constant, deliming and pickel phases should be standardized.

As for temperature, if the desired pH value is reached in a reasonable timescale, chromium can unfold its optimum responsiveness for a longer duration and, consequently, increase the efficiency of fixation.

Masking

Masking agents, besides facilitating the penetration of chromium, making it more stable to precipitation with alkali and giving leather blue-tinted shades and a finer grain, can swell the molecule of tanning.

This means that the reticular complex of chromium can more easily and consequently improve the efficiency of fixation and of exhaustion of the float.

CONCLUSION

By optimizing the above listed parameters according to the recommended guidelines the overall depletion of chrome can be greatly improved. Furthermore, they could reduce the concentration of tanning agent in wastewater of the whole cycle of over 80 mg/l¹

¹ Calculated assuming the use for each kilogram of raw skin of 25 liters of water for a complete processing cycle, an average content of 3000 mg/l of sulfates of 7000 mg/l of chloride and 200 mg/l Cr in the effluent at the end of the process.

Courtesy

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