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Regional Programme for Pollution Control in the Tanning Industry in South-East Asia

CHROME MANAGEMENT IN THE TANYARD

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1. INTRODUCTION

Chrome tanning is the most common type of tanning in the world. Chrome tanned leathers are characterized by top handle quality, high hydrothermal stability and additional user properties including a versatile applicability. Waste chrome from leather manufacturing poses a significant disposal problem.

Waste chrome occurs in three forms:

- Liquid waste: This form includes mainly spent floats from tanning, sammying, draining and retanning.
- Sludge: This is produced by mixing and balancing total tannery wastewater streams in the primary stage of an effluent treatment plant.
- Tanned waste: This occurs in the form of shavings, trimmings, buffing dust and unusable split, mostly in wet blue, but also in crust and finished leather.

The regulation of chrome discharge from tanneries is worldwide. Nowadays, all tanners must check their waste streams. Chrome is a component that has to be strictly controlled.

Environmental impact of chrome discharged from tanneries has been a subject of extensive scientific and technical dispute. However, the respective legislative limits to chrome discharge and disposal, and the relevant guidelines are valid and adopted all over the world.

Limits to the total chrome discharged in effluent vary in a broad range of 0.05 - 10 mg/l in case of discharging into water bodies (direct discharge) and 1-50 mg/l in case of discharging into the sewer (indirect discharge) (1).

Chrome containing sludges are mostly disposed of in landfill which have to be provided with a leachate collection and treatment system. In case of land application of sludges, very strict limits have been adopted in most European countries (2). Typical parameters monitored are: initial chrome concentration in the soil (mg Cr/kg dry soil), Cr content in the sludge (mg Cr/kg of dry sludge), cumulative (maximum) chrome loading during a 10 year-period (kg Cr/hectare). Specific values for European countries and the USA are presented in Annex 1.[1]

Some tanned wastes are partly utilized in by-products, but most are deposited in landfill. Blue shavings and trimmings are utilized by processing in leatherboard manufacture, by chemical and/or enzymatic hydrolysis, pyrolysis, and incineration (3).

Due to the noted relevance of chrome tanning to the environmental impact of leather manufacturing, the chrome management in a tannery is of primary importance. Therefore, this paper aims to disseminate updated information on chrome management and most frequently practised techniques of reducing the chrome amount in tannery wastewater. The provision of updated information and practical experience will likewise aid in expanding leather manufacture without causing unnecessary damage to the environment.

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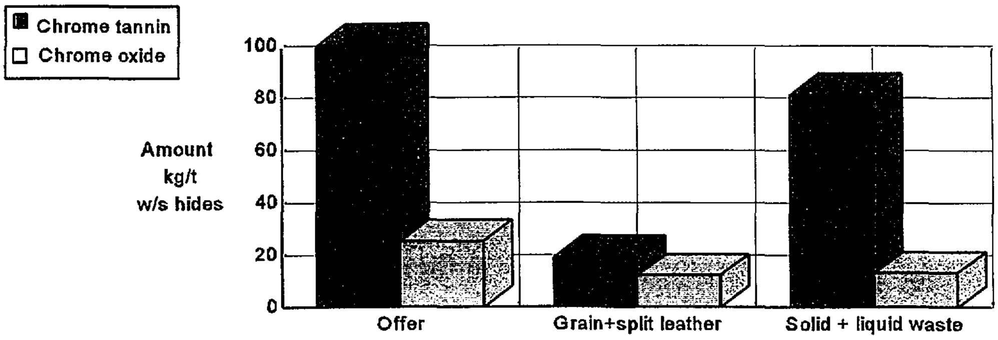
[1] *For example, France limits chromium content in the soil to150 mg/kg dry soil, 1,000 mg chromium/kg dry sludge and the total cumulative chrome loading to 360 kg chrome/ha. Exceptionally strict limits are found in Denmark and Sweden (100-150 ppm in dry sludge).*

2. CONCERNS OF CHROME MANAGEMENT

The primary concern of a tanner in chrome management is the balance of the chrome remaining in grain leather and split, that contained in solid waste, and that discharged in effluent. A typical balance is shown in Figure 1.

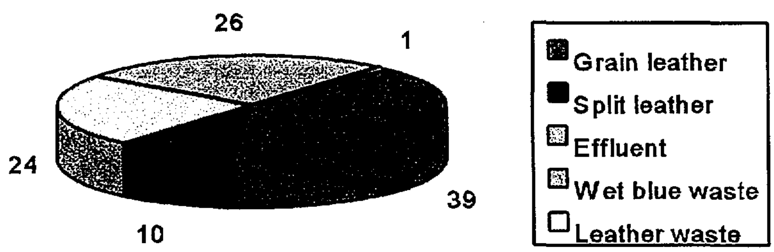
Figure 1
Chrome Balance in Leather Manufacture according to (4)



The balance is based on a generally applied chrome tannin containing 25 % Cr_2O_3 and neutral salts. The balance is calculated on the use of 2 % Cr_2O_3 on pelt weight for tanning and 1.2 % Cr_2O_3 on shaved weight for retanning. There is also an assumption that chrome reacts with pelt collagen in the form of basic chrome sulphate in these models.

The share of chrome oxide distributed in leather and individual waste streams is illustrated in Figure 2.

Figure 2
Chrome Oxide Distribution in Leather and Waste in %



It follows from the balance that less than 50 % Cr_2O_3 of the input is found in leather (grain + split) while more than 50 % Cr_2O_3 is disposed in solid and liquid waste streams. That is why chrome tanning processes and solid/liquid chrome wastes should be of prime concern.

2.1. Chrome Management in Tanning Processes

Pickling, tanning, sammying, draining and post tanning operations are concerns of chrome management. The amount of chrome discharged in effluent processing 1 tonne of wet salted hides may be summarized as follows (5):

Tanning	2 - 5 kg Cr/t
Post tanning	1 - 2 kg Cr/t
Total	3 - 7 kg Cr/t, i.e.
	5 - 10 kg Cr_2O_3/t

An example of the chrome amount discharged in effluent from individual operations under standard technological conditions is shown in Table 1.

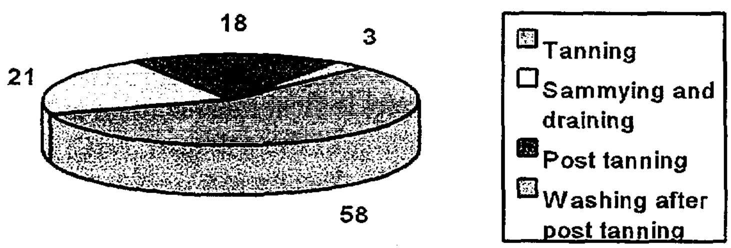
Table 1
Chrome Discharged in Effluent from Individual Operations

Operation	Cr_2O_3 kg/t w/s hides
Offer	21
Discharge - spent tanning float - sammying and draining floats - post tanning floats - washing float after post tanning - total	 4.1 1.5 1.3 0.2 7.1
Utilization %	66

The example given above is being found among many possible cases in practice. In general, chrome uptake under typical technological conditions is within 60 - 80 % of the offer.

The share of chrome oxide discharged in effluent from individual operations is illustrated in Figure 3.

Figure 3
Share of Chrome Oxide Discharged in Effluent from Individual Operations under Standard Technological Conditions in %



Data in Figure 3 substantiate that the main portion of chrome discharged comes from the tanning float while another significant portion of chrome is discharged from spent retanning floats.

Hence, the chrome management has to be focused on all operations in the tanyard and the wet finishing department. Maximizing the chrome uptake should be the first priority in any chrome managing project. High exhaustion chrome tanning reduces not only the chrome concentration in spent tanning floats but also the chrome losses to effluent owing to high chrome fixation in crosslinked collagen.

A special concern of chrome management in tanning processes is chrome replacement. Practical experience shows that no metal tanning agent will match chrome (III) in its versatility. Total chrome replacement is possible if lesser hydrothermal stability and handle qualities are acceptable. However, the majority of leather end uses require the high hydrothermal stability. For example, shoe upper leather must withstand hot lasting and heat setting while garment leather must withstand steam pressing.

The concept of wet white is regarded as an alternative. The pelt may be pretanned by aluminium/titanium salts, silicon dioxide gel, polyacrylates, syntans, aldehyde derivatives or other tanning agents (6). The wet white product with a partly stabilized structure can be split, if this has not been done after liming, shaved and trimmed. After mechanical processing, the main chrome tanning is carried out. In this tanning, only approximately 9.5 kg Cr_2O_3/t w/s hides is needed in comparison to a conventional 21 kg Cr_2O_3/t (7). The advantage is primarily a saving of chrome and minimizing the production of chrome tanned waste. However, wet white technology has so far found limited practical use and commercial acceptance.

2.2. Waste Chrome Management

The management of waste chrome should not be neglected either. The amount 3 - 7 kg Cr/t wet salted hides discharged under standard technological conditions represents a concentration of 60 - 140 mg Cr/l in mixed wastewater streams when considering the water consumption of 50 m^3/t w/s hides. This concentration is not acceptable in many countries with their legislative limits for direct/indirect effluent discharging and limits for sludge landfilling. That is why any chrome managing project has to deal with the problem of reducing the chrome concentration in effluent not only by maximizing the chrome exhaustion in tanning, but also by additional methods, e.g. chrome tanning floats recycling and chrome recovery/reuse.

3. IMPROVEMENT OF CHROME TANNING PROCESS

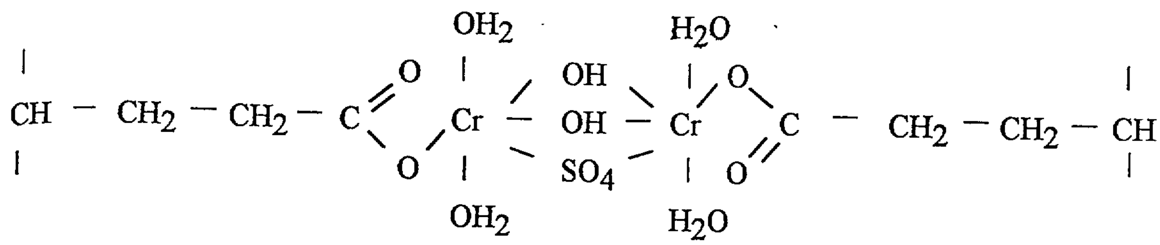
The standard chrome tanning process can be roughly divided into three phases, namely pickling, tanning, and basification. Previously these phases were kept separate from each other and carried out one after the other. Nowadays they often overlap.

Pickling

Pelts are acidified in a salt solution. A combination of sulphuric and formic acid is frequently used in an amount of 1.0 - 1.8 % on pelt weight. Another combination is with sulphuric acid and sodium formate. The pickle float must contain at least 5 % neutral salts on pelt weight in order to prevent acid swelling of the collagen. NaCl is generally used for this purpose. Under standard conditions, 40 - 60 % float on pelt weight is applied, pickling time 1-2 hr, float pH 2.8 - 3.0.

Tanning

Reaction sites for chrome tanning are the ionized carboxyl groups on side chains of the collagen. The lateral crosslinking of chrome complexes was suggested, e.g.



In this structure the chrome complexes are bound on side chains of glutamic acids. Similarly, they can be bound on side chains of aspartic acids.

Tanning starts in the pickling float. Most commercial chrome tannin products in powder form are applied containing about 25 % Cr_2O_3 of 33 % basicity. Basic chrome sulphate liquors are also used. These liquors are prepared by reduction of Na/K dichromates in the presence of sulphuric acid. The reduction is carried out, as a rule, with sulphur dioxide or technical sugars.

The corresponding chrome offer in tanning is usually 1.5 - 2.5 % Cr_2O_3 on pelt weight. Under standard conditions, 60 - 80 % float on pelt weight is used.

Basification

Basification is done during the tanning operation in order to neutralize pickling acids and any acid produced in the reaction with the collagen. At the same time the reactivity of chrome complexes is enhanced due to their continuously increasing basicity of 33 % up to 66 % at the end of tanning.

Sodium hydrogen carbonate is often used as a basification agent. Usually it is dosed towards the end of tanning in several portions in a total amount of 0.8 - 1.2 % on pelt weight in order to achieve the final pH 3.8 - 4.2 in the float. Magnesia as a self basifying agent containing 60 % MgO may also be used. Due to its low solubility, this agent reacts very slowly with acids. It can be added at the start of tanning in an amount of 0.6 - 0.8 % on pelt weight, gradually increasing the float pH up to 3.8 - 4.2. Chrome tannins containing a self basifying component based on MgO or dolomite are commercially available as well. In that case the basification agent need not be added separately. In a conventional procedure the tanning and basification operation should be finished at a float temperature of 35 - 40 ^{o}C. The drumming time should be at least 6 - 8 hours. The chrome concentration in spent float, as a rule, is in a range of 3.5 - 7.0 g Cr_2O_3/l. After the drumming, leather will be unloaded, drained and sammed.

To improve the chrome tanning process, above all the chrome uptake has to be increased to decrease the chrome concentration in residual floats as much as possible. There are two main approaches to increase the chrome uptake in the tanning process:

- Optimizing process parameters
- Modifying tanning process

Both approaches offer various options of increasing the process efficiency.

3.1. Optimizing Process Parameters

Mechanical action, concentration of chrome and its offer, pH, temperature and reaction time are main parameters to be optimized in order to increase the process efficiency, improve the chrome uptake and decrease/minimize the chrome concentration in effluent.

3.1.1. Mechanical Action

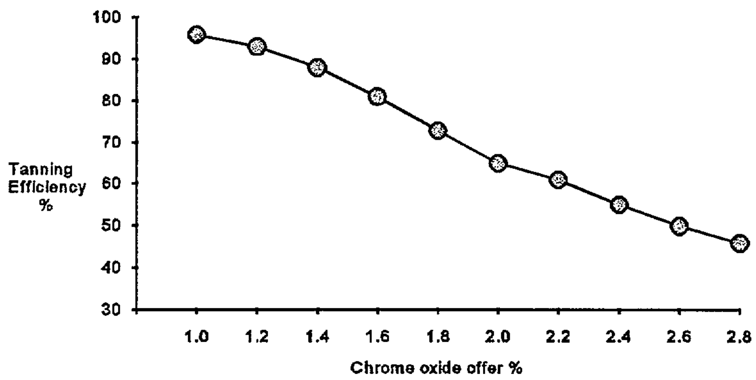
Agitation in the drum is a mechanical action that is the prime mode of transporting chemicals into the substrate. In case of chrome tannins, a sufficient intensity of an agitation is indispensable both for good penetration of chrome and for achieving the time necessary to complete the reaction of the whole system. The intensity of agitation is determined above all by the drum speed. In practical terms for an optimum mechanical action the speed of drum rotation should be about two thirds of the critical rate (6).

3.1.2. Concentration and Chrome Offer

The efficiency of chrome tannin uptake depends on the concentration in the solution, which is decisive for the course of diffusion. The higher the chrome concentration in the float, the faster the chrome penetrates into the fibre structure. Likewise, as the concentration reduces, the rate of the reaction between collagen and chrome will be decreased. The penetration is a precondition for the final through-reaction in all layers of the pelt. All recipes of a tanning process address this fact and prescribe a certain excess offer of the tannin agent for safety quality reasons. However, this always causes problems with chrome and other chemicals that remain in spent floats.

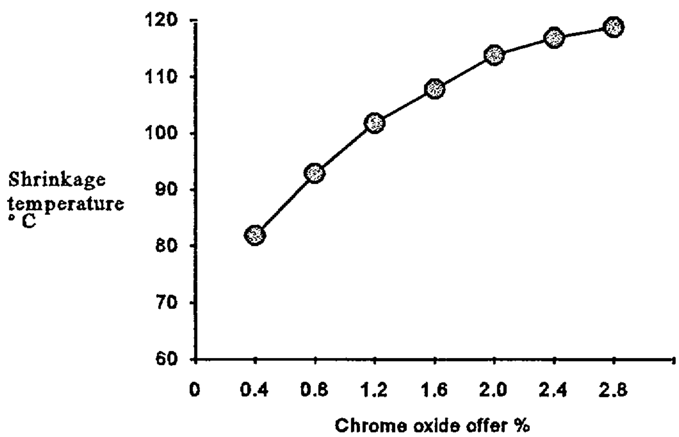
Chrome in the form of a binuclear basic chrome sulphate reacts quite specifically with ionised carboxyl groups of the collagen. The efficiency of chrome tanning, defined as a proportion of the chrome offer that has been fixed to the collagen, is illustrated in Figure 4.

Figure 4
Efficiency of Chrome Tanning as a Function of Cr_2O_3 Offer according to (6)



Under standard conditions, the efficiency of chrome tanning and the simultaneous exhaustion of chrome from the float increases when the chrome offer decreases. However, there is a limit to reducing the chrome offer with respect to the shrinkage temperature. The effect of chrome offer on shrinkage temperature is shown in Figure 5.

Figure 5
Effect of Chrome Offer on Shrinkage Temperature (°C) according to (6)

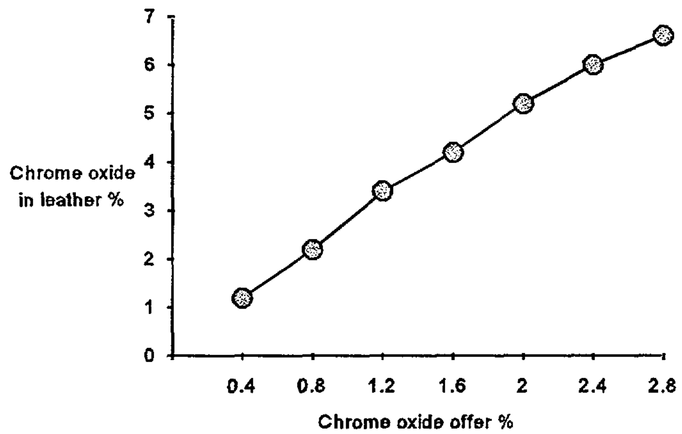


Approximately 2% Cr_2O_3 is sufficient to achieve a shrinkage temperature of 110°C and higher, which affects the boilfastness of leather. An additional increase of the chrome offer is of no practical benefit. At a level of 2 % Cr_2O_3 offer only the 65 % efficiency of chrome tanning may be reached (see Figure 4) , whereas in practice efficiency of 60-80 % is achieved.

The shrinkage temperature of 100°C can actually be reached at a level of about 1 % Cr_2O_3 offer. But in practice under normal conditions, when one applies a chrome offer lower than 1.6 - 1.7 % Cr_2O_3, it may be difficult to achieve the leather boilfastness and obtain the uniform distribution of chrome through the leather cross-section (8).

If the chrome offer increases, the chrome content in leather will increase as well, as shown in Figure 6.

Figure 6
Effect of Chrome Offer on Chrome Content in Leather according to (6)



Leather tanned with an offer of about 2 % Cr_2O_3 contains 4 - 5 % Cr_2O_3. In practice, a chrome content of about 3.5 % Cr_2O_3 is needed in order to achieve the shrinkage temperature of 100°C (8).

For quality reasons, when applying a standard tanning procedure, the tanner has to be careful to minimise the chrome offer and reduce the chrome concentration in effluent. The tanner should make an effort to optimize other process parameters and/or modify the tanning process when aiming at a reduction of the chrome concentration in effluent, without impairing the performance and quality of the leather.

3.1.3. Reaction Time, pH and Temperature

The tanning 1.reaction is an equilibrium system. The increase of reaction time means that the reaction will finish closer to the point of equilibrium, i.e. a longer process time results in more chrome fixed on the collagen.

Under constant conditions, the chrome content in leather and the shrinkage temperature increase with the tanning time (9). A more efficient chrome uptake, increased chrome content in leather and shrinkage temperature can also be achieved at higher pH values. The effect of pH on the tanning reaction is associated with the pH influence on chrome species. It is known that chrome complex of 33 % basicity has pH 2.8 in solution and contains mostly binuclear species while a solution of chrome complex of 50 % basicity has pH 3.5 and contains more adstringent trinuclear and larger ions.

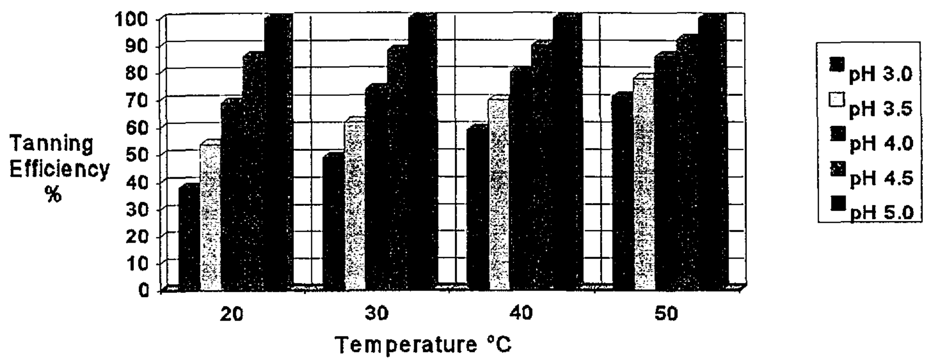
It is important to recognise the differences between pH and temperature, with regard to their influences on chrome fixation and the corresponding shrinkage temperature. Increasing either the temperature or the pH of a chrome tannage will always increase chrome fixation and it is generally true that increasing the chrome content of a leather will increase the shrinkage temperature. But, it should be remembered that temperature increase primarily controls chrome fixation and that pH increase primarily controls shrinkage temperature rise.

Furthermore, the relationship between chrome uptake and shrinkage temperature depends on how the tanning reaction is conducted, that is the timetable for temperature and pH rise during the tannage.

- The earlier heating is started, the higher the chrome uptake will be, or in other words, the later heating is applied, the lower the chrome uptake will be.
- The heating timetable has little or no effect on the shrinkage temperature achieved. Conversely, the basification timetable has little or no effect on the chrome uptake.
- Early basification is likely to produce a lower shrinkage temperature, but late basification will have neither a positive nor negative effect on shrinkage temperature.
- Maximum shrinkage temperature is achieved by slow, regular increments in pH rise during basification.

In an effort to increase the chrome uptake and reduce the chrome concentration in effluent, tanners have a tendency to carry out the tanning process at elevated pH and temperature. The problem is to maintain the reaction between chrome complex and collagen and to avoid chrome precipitation. Changes of the tanning efficiency with respect to the final float pH and temperature are exemplified in Figure 7. The results are taken from a series of graphs which indicate effectively 100% efficiency at pH 5.0 at all temperatures (6,11).

Figure 7
Effect of Final pH and Temperature (°C) on Tanning Efficiency in % of Chrome Offer Fixed on Collagen



By slow and very careful basification it is possible to basify to pH 5.0 without causing chrome staining in order to achieve the highest chrome uptake. However, for commercial application such a procedure should not be recommended without applying high degrees of process monitoring and control system.

To sum up possibilities of optimizing parameters of the chrome tanning process in view of required leather quality and the decrease of the chrome concentration in effluent, a survey according to (6) is presented in Figure 8.

Figure 8
Factors to be Optimized in Chrome Tanning Process

Level decreased
Chrome offer
Rate of pH and temperature changes

Level increased
Mechanical action
Temperature
pH
Reaction time

Many years' experience has provided the following knowledge:

- Better chrome uptake and reduced chrome concentration in effluent can be achieved by finishing the tanning at the highest possible pH and temperature. End values up to 40 - 45°C and pH 4.0 - 4.2 are advantageous.
- Benefits will be obtained by using the least amount of chrome offer combined with the high chrome concentration in the float, the tanning time as long as possible, and with fast running. A chrome offer lower than 1.7 % Cr_2O_3 is not recommended for commercial application.

3.2. Tanning Process Modifications

Modifications to improve the chrome uptake and to reduce the chrome concentration in effluent involve above all masking the chrome tanning complex and increasing the collagen reactivity. All the modifications are usually combined with an optimization of tanning process parameters. The combination of process modifications and the optimization of process parameters is the basis of a modern, environment friendly high exhaustion chrome tanning process.

3.2.1. Masking in Chrome Tanning

Masking is defined as incorporation of certain reactive groups, i.e. ligands, into chrome tannin complexes. The purpose of masking by monobasic salts is to enhance the chrome penetration rate and enable basification to higher pH, i.e. to increase the pH value at which the chrome complex precipitates. Crosslinking masking salts can enhance chrome reactivity but reduce penetration rate.

Dicarboxylic acids are the well known masking agents. Short chain dicarboxylic acid salts will produce cyclic, chelate complexes if the ring size is 5-7 membered; this will reduce the reactivity of chromium (III). Longer chain dicarboxylic acid salts will crosslink two chromium (III) molecular ions; this makes the chrome species bigger, increasing reaction rate but decreasing penetration rate. By the inclusion of an organic acid, the complexes are less cationic and this acts as a reduction of the adstringency or affinity to the collagen. The masked chromium salt penetrates more easily through the substance. The chrome distribution over the cross-section is more uniform. Nowadays masked chrome tannins are commercially available. Tanning liquors with a low degree of masking are produced when acid dichromate is reduced with molasses.

There are several other tanning auxiliaries available in the market, usually based on some cross-linking function, e.g. aliphatic dicarboxylates, low molecular weight polyacrylates and syntans. They may be applied at the start of tanning or even form a part of the basification system. Another example refers to the use of a mixture of aliphatic dicarboxylic acids in the pickle and sodium aluminium silicate for the basification (6). A more recent development is to complex weakly or unbound chrome by applying low molecular weight polyacrylates in tanning or in retanning (8).

3.2.2. Increasing Collagen Reactivity

The main way of increasing the collagen reactivity is to increase the number of carboxyl groups on the amino acid side chains in order to produce more sites available for crosslinking. To this purpose glyoxylic acid was suggested to condense additional carboxyl croups into the collagen using the Mannich reaction (12).

Glyoxylic acid has been determined to be an aid to tanning when used in the pickle prior to the chrome tanning. By converting amine groups to carboxyl groups additional sites are created for the chrome to react with the collagen. The chrome offered is better exhausted and more strongly fixed than in a conventional tanning. Tanning auxiliaries on the basis of glyoxylic acid are commercially available too.

3.2.3. Efficiency of High Exhaustion Tanning

For a better illustration here are some examples of high exhaustion tanning procedures and their effects on reducing the chrome amount in residual floats.

Example 1: Masking in chrome tanning

- Pelt: Grain split 3.2 mm.
- Pickle: Common salt, formic and sulphuric acid, 20 - 40 % water, 20°C, 80 min.
- Tannage: 33 % basic chrome sulphate containing 26 % Cr_2O_3, run 60 min, high reactive organically masked self-basifying chrome tannin with 7 % Cr_2O_3, run 8 hr, final temperature 42°C.

Results of a high exhaustion tanning process according to the Example 1 compared to a conventional chrome tanning are obvious from Table 2.

Table 2
Chrome Concentration in Residual Floats from High Exhaustion and Conventional Tanning Process according to (13)

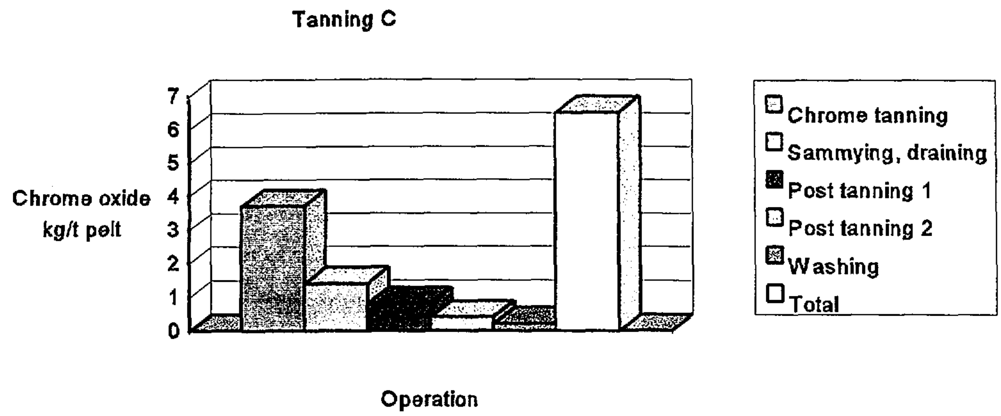
Tanning C - conventional, 1.9 % Cr_2O_3 on pelt weight
Tanning HE - high exhaustion, 1.3 % Cr_2O_3 on pelt weight

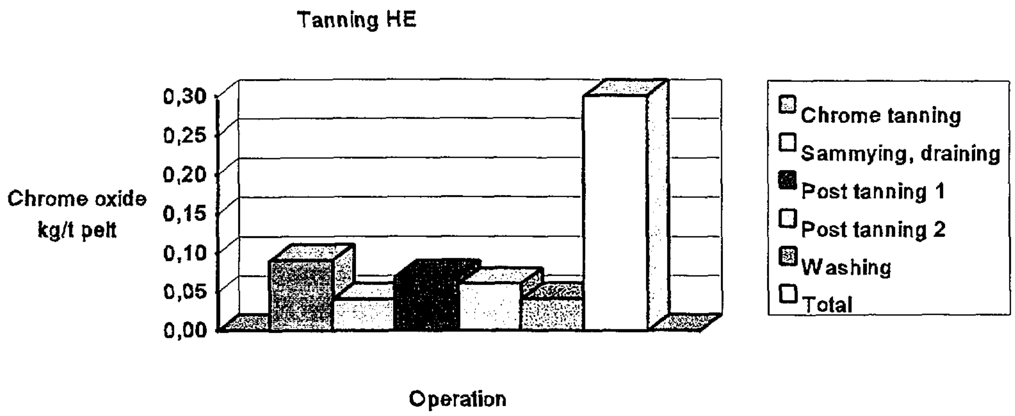
	Tanning C		Tanning HE	
	pH	g Cr_2O_3/l	pH	g Cr_2O_3/l
Chrome tanning	3.6	6.99	4.2	0.30
Sammying	-	5.99	-	0.19
Post tanning 1	4.5	1.01	4.6	0.11
Post tanning 2	3.8	0.49	4.1	0.09
Washing	3.9	0.11	4.1	0.02

After recalculating the figures given in Table 2 with respect to float volume, one may compile the following balance of unused chrome (Figure 9):

Figure 9
Unused Chrome in Residual Floats from High Exhaustion and Conventional Tanning Process According to (13)

Tanning C - conventional, 1.9 % Cr_2O_3 on pelt weight
Tanning HE - high exhaustion, 1.3 % Cr_2O_3 on pelt weight





It follows from Figure 9 that the chrome utilization in a high exhaustion tanning process is increased up to 98 % while for conventional tanning a utilization of 66 % is characteristic. The higher chrome utilization causes the significantly lower chrome concentration in residual floats. Using a high exhaustion tanning procedure the chrome leaching is minimum. Leathers from both conventional tanning with a chrome offer of 1.9 % Cr_2O_3 and high exhaustion tanning with a chrome offer of 1.3 % Cr_2O_3 contain approximately the same amount of chrome in the range 4.0 - 4.5 % Cr_2O_3.

Example 2: Increasing collagen reactivity

- Unsplit pelt
- Pickle: Common salt, glyoxylic acid, formic and sulphuric acid, 20 - 40 % water, 25°C, 4 hours
- Tannage: 33 % basic chrome sulphate with 26 % Cr_2O_3, 1 - 4 hours, MgO, 1 - 2 hours, temperature increased slowly to 45 - 55°C. Total running time after basification 6 hours, final pH 3.9 - 4.2.

Results of a high exhaustion tanning process according to the Example 2 compared to a conventional chrome tanning are shown in Table 3.

Table 3
Chrome Concentration in Residual Floats from High Exhaustion and Conventional Tanning Process according to (12)

Tanning C - conventional, 2.0 % Cr_2O_3 on pelt weight
Tanning HE - high exhaustion, 1.4 % Cr_2O_3 on pelt weight

Residual float	Concentration g Cr_2O_3/l	
	Tanning C	Tanning HE
Chrome tanning	5.55	1.04
Sammying	3.44	0.58
Washing 1	0.19	0.02
Neutralization	0.02	0.01
Washing 2	0.01	0.01
Retanning, dyeing, fatliquoring	0.03	0.01
Washing 3	0.02	0.01

The implementation of a procedure with the increased collagen reactivity after adding glyoxylic acid in the pickle results in very high exhaustion of the tanning float and very good chrome fixing in the leather as well. One may reduce the chrome offer in the range 1.0 - 2.0 % Cr_2O_3 depending on the pelt thickness without any change in the chrome content in leather (4.0 - 4.5 % Cr_2O_3) and in the boilfastness.

Example 3: Final pH and temperature

A relation between the final pH/temperature value and the chrome concentration in the residual tanning float is demonstrated in Figures 10 and 11.

Figure 10
Effect of Final pH on Chrome Concentration in Residual Float from High Exhaustion Tanning Compared to Conventional Tanning according to (14)

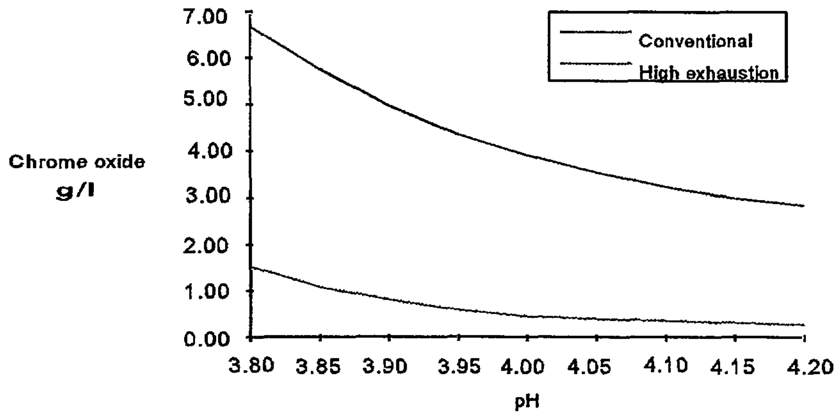
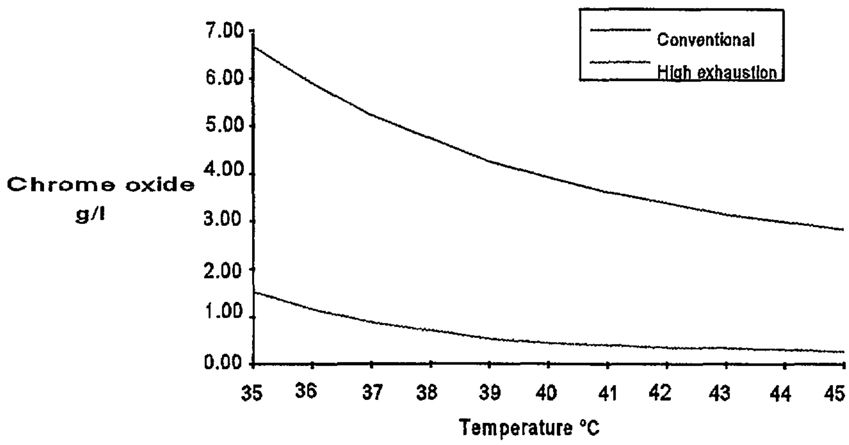


Figure 11
Effect of Final Temperature (°C) on Chrome Concentration in Residual Float from High Exhaustion Tanning Compared to Conventional Tanning according to (14)



It follows from Figure 10 that to achieve the lowest chrome concentration in the residual tanning float the basification should be directed to a final pH value at least 4.0. For the same reason the whole process should be finished at a temperature min. 40°C (Figure 11). These conclusions are accepted for conditions of a conventional tanning as well.

Example 4: Chrome fixing in post tanning

The chrome concentration in residual floats from post tanning when using special polyacrylate dosed prior to the neutralization is shown in Table 4.

Table 4
Chrome Concentration in Residual Floats from Post Tanning with/without Polymer Fixing according to (15)

Residual float	Concentration mg Cr/l	
	Without fixing	With fixing
Washing 1	550	-
Washing 2	430	-
Neutralization/retanning	320	11
Washing 3	-	14
Fatliquoring/dyeing	218	11
Washing 4	83	7

It results from Table 4 that after fixing the chrome with special polymer acrylate the chrome concentration in residual floats is around 10 mg/l, while it ranges within 200 - 500 mg/l when a conventional post tanning procedure is applied. The chrome fixing in post tanning decreases the chrome discharge from post tanning operations in effluent to a value of less than 0.4 kg Cr/t w/s hide (16).

Example 5: West European experience

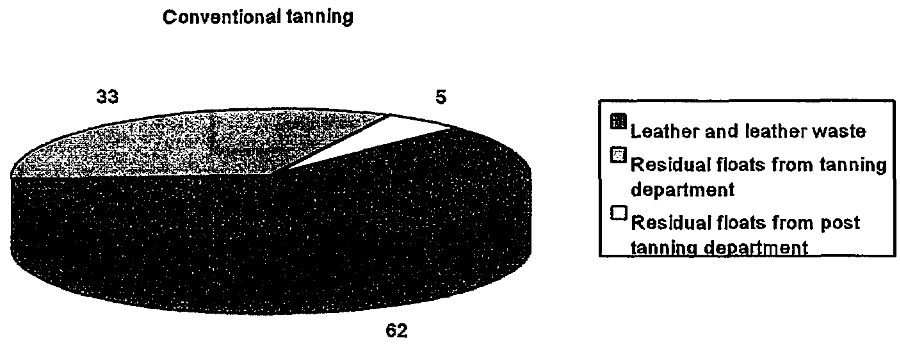
Some practical experience from West European tanneries has been collected and evaluated with respect to the tanning efficiency (7, 16). Results of the evaluation are compiled in Table 5 and graphically illustrated in Figure 12.

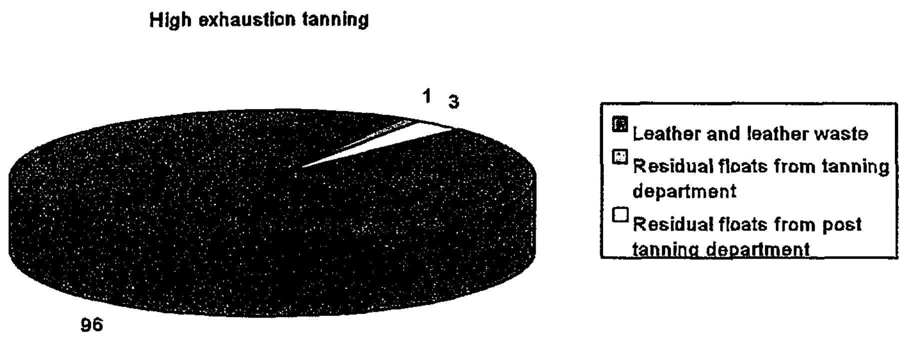
Table 5
Efficiency of High Exhaustion Chrome Tanning Process Compared to Conventional Process according to West European Experience

Tanning C - conventional
Tanning HE - high exhaustion

Chrome amount kg Cr/t w/s hides	Tanning C	Tanning HE
Offer	15.5	10.0
Leather and leather waste	9.6	9.6
Residual floats from tanning, draining, sammying	5.2	0.1
Residual post tanning float	0.7	0.3

Figure 12
Share of Used/Unused Chrome in % in High Exhaustion Process Compared to Conventional Process





Experience in West European tanneries substantiates the attainability of a very high chrome exhaustion using new tanning procedures. This very high exhaustion results in discharging only 4 % of the chrome offer while in a conventional tanning 10 times more chrome is discharged. The chrome offer can be reduced by 35 % and thus chrome tanning materials can be saved .

The amount 0.4 kg Cr/t w/s hides (Table 5) represents an average concentration of 13 mg/l in mixed wastewater streams when assuming water consumption max. 30 m^3/t w/s hides in a modern tannery. The attainment of this concentration facilitates wastewater handling by direct/indirect effluent discharging and sludge landfilling according to local legislative limits.

4. CHROME RECYCLING

To recycle spent floats from chrome tanning directly back into processing is the simplest way of chrome reuse.

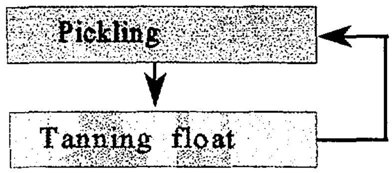
4.1. Recycling Technique

Several recycling techniques are employed industrially (16):

Option A

Spent tanning float is recycled to pickling in the next run (Figure 13).

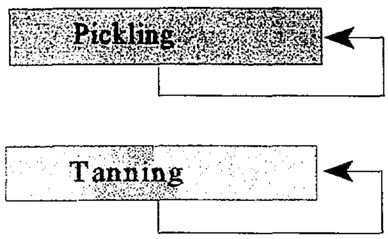
Figure 13
Recycling of Spent Tanning Float to Pickling



Option B

Pickling and tanning are operated in separate floats. Both floats are recycled in the next run (Figure 14).

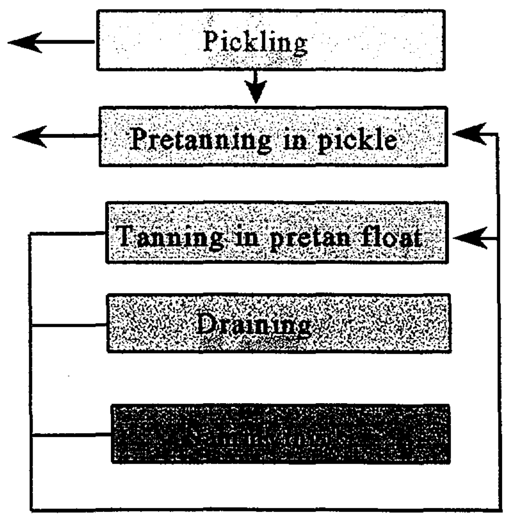
Figure 14
Separate Recycling of Spent Pickling and Tanning Floats



Option C

A pretanning operation is placed between pickling and tanning. Spent tanning float mixed with drain and samm water are recycled in the next run of pretanning and tanning. A part of pickling and pretanning floats are discharged daily (Figure 15).

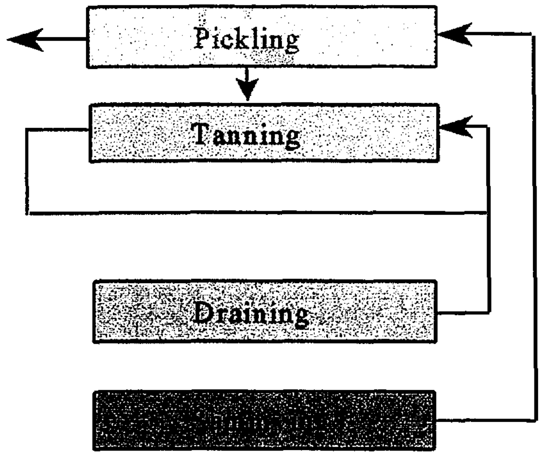
Figure 15
Recycling of Tanning Floats to Pretanning and Tanning



Option D

Spent tanning float mixed with drain water is recycled in the next run of tanning. Samm water is recycled in the next run of pickling and discharged daily (Figure 16).

Figure 16
Separate Recycling of Spent Tanning Floats and Samm Water



Other modifications of recycling techniques are applied in practice too. In all cases leather fibres and other undissolved impurities must be removed by filtering the recycled floats. The implementation of any recycling technique in tanning operations calls for the installation of storage tanks, pumps, filters etc., which are commercially available in the market.

A technological basis of the chrome recycling was established by Davies and Scroggie (17). They demonstrated the importance of controlling and adapting the ionic strength of recycled floats to avoid acid swelling and reaching equilibrium in the chemistry system after several cycles.

Neutral salt build up occurs, as a rule, over 5 cycles and then reaches a steady state. Furthermore, it follows from experimental data that an accumulation of less reactive or inactive chrome complexes does not occur in the course of recycling tanning floats. This is why the tanning process should not be negatively affected by recycling floats.

The float volumes balance in chrome recycling causes some problems. The float volume needed in the pickle is lower than the volume of spent tanning float including drain/samm water. This follows from the fact that the spent float discharge after deliming and bating is incomplete and the water content in pelt is higher (70 %) than in wet blue (55 %). The addition of pickle acids, dissolved chrome tannins and basifying agents increases the volume of recycled spent floats as well.

In practice, there is usually more float available to be recycled than can be used (6). This excess float must be discharged to effluent or treated in order to recover the chrome by precipitation. Optionally, it might be used in retanning. In a high exhaustion tanning process the spent tanning float can be recycled to form the whole volume of the pickling float. In this way there is no excess volume build up.

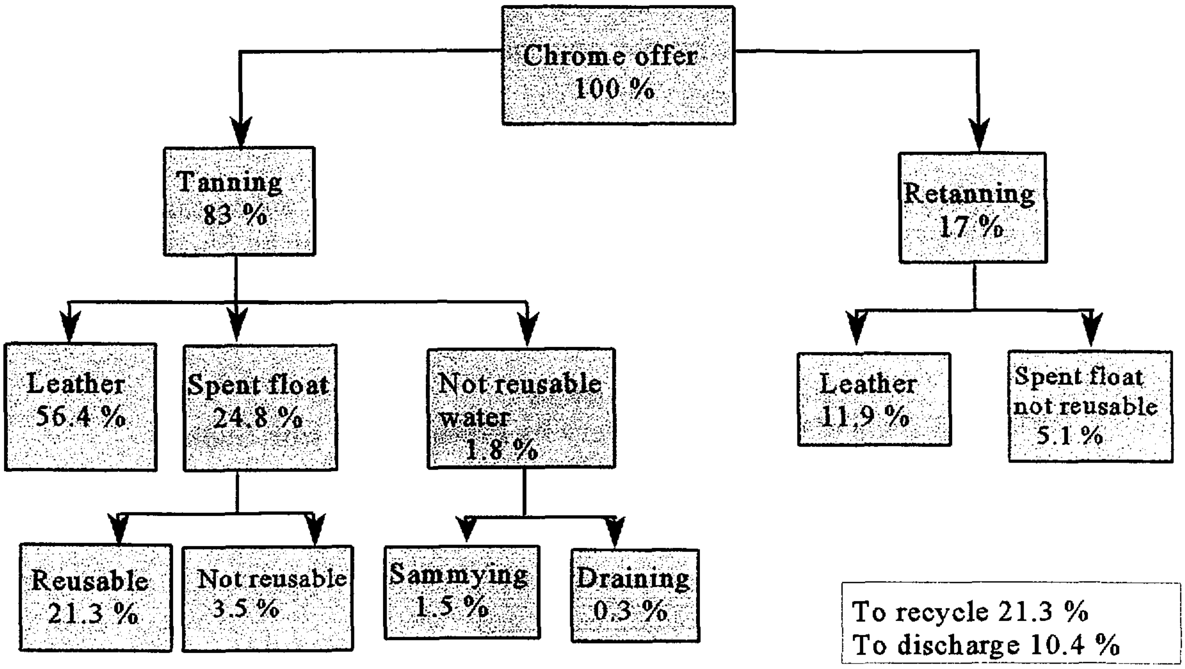
4.2. Recycling Efficiency

Chrome distribution between the leather and spent floats has been presented with respect to direct reuse by recycling (6). Data related to the chrome tanning/retanning efficiency of 68% are presented in Table 6 and Figure 17.

Table 6
Chrome Distribution between Leather and Spent Floats with Respect to Direct Chrome Reuse by Recycling

Chrome	Distribution %
Offer	
- total	100
- tanning	83
- retanning	17
Leather	
- total	68.3
- tanning	56.4
- retanning	11.9
Spent tanning float	
- reusable	21.3
- not reusable	3.5
- total	24.8
Residual water not reusable	1.8
- sammying	1.5
- draining	0.3
Spent retanning float	
- not reusable	5.1
Total	
- to recycle	21.3
- to discharge	10.4

Figure 17
Chrome Distribution Scheme
Direct Chrome Reuse by Recycling
Tanning/Retanning Efficiency 68 %



Some other models of a chrome distribution can be constructed as well. The model in Table 6 and Figure 19 demonstrates one possible case. It follows from this model that 21 % of the chrome offer can be reused and saved by means of direct recycling spent floats. Considering the standard offer 2.0 % Cr_2O_3 on pelt weight, i.e. 2.2 % Cr_2O_3 on w/s weight, and water consumption 50 m^3/t hides, 10 % of chrome offer to be discharged means the concentration in mixed wastewater streams is 30 mg Cr/l. According to the model, 90 % uptake of the chrome offer is reached by a recycling technique. Then the chrome load discharged in effluent will be decreased to 1.5 kg Cr/t w/s hide.

The recycling efficiency depends above all on the completeness of float collection, the rate of float excess to be discharged daily and the recycling technique used. The 90 % efficiency means a standard that is easily attainable when recycling the floats from a conventional chrome tanning. Better collection and more sophisticated recycling technique facilitates attaining 95 - 98 % efficiency. Then the chrome load discharged in effluent will be decreased to 0.30 - 0.75 kg Cr/t w/s hides. In this case the chrome concentration in mixed wastewater streams may be assumed to be in the range 10 - 25 mg Cr/l for water consumption at 30 m^3/t hides.

5. CHROME RECOVERY

To recover the chrome from spent tanning floats after precipitation is an indirect way of recycling and reusing the chrome in processing. Indirect chrome reuse after the precipitation of residual tanning floats enables the tanner to avoid a problem of increasing float volume. In some cases of the precipitation of chrome from floats, the recovered chrome is not being reused but only dumped.

5.1. Recovery and Reuse

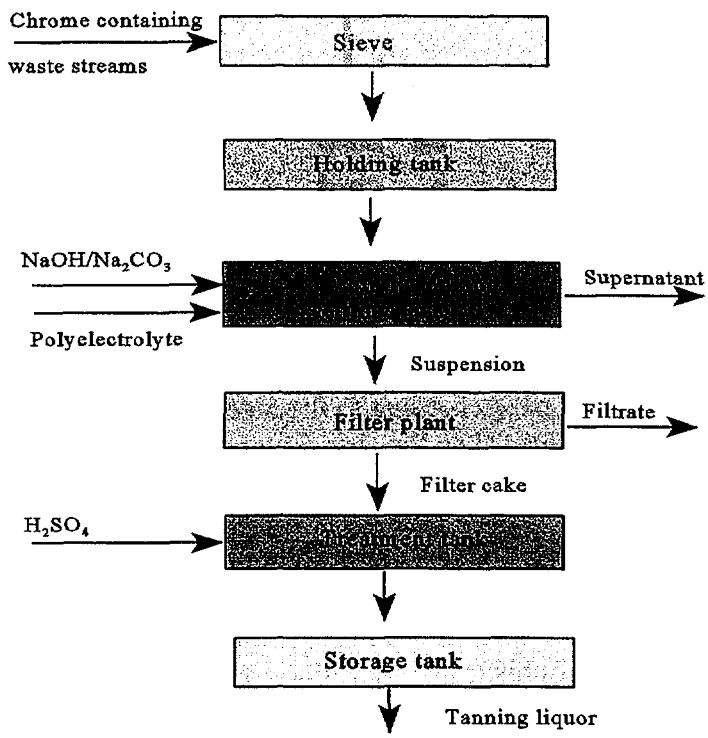
5.1.1. Recovery/Reuse Technique

The principle consists in recovering the chrome from residual chrome containing floats by precipitation, separation, then redissolving it in acid for reuse. Variations arise in the base used to precipitate the chrome. There are two principal options:

Option A

Fast precipitation with sodium hydroxide or sodium carbonate, aiding coagulation with polyelectrolyte, then thickening and dewatering the voluminous sludge by filtration. A simple flow diagram of this recovery system is shown in Figure 18.

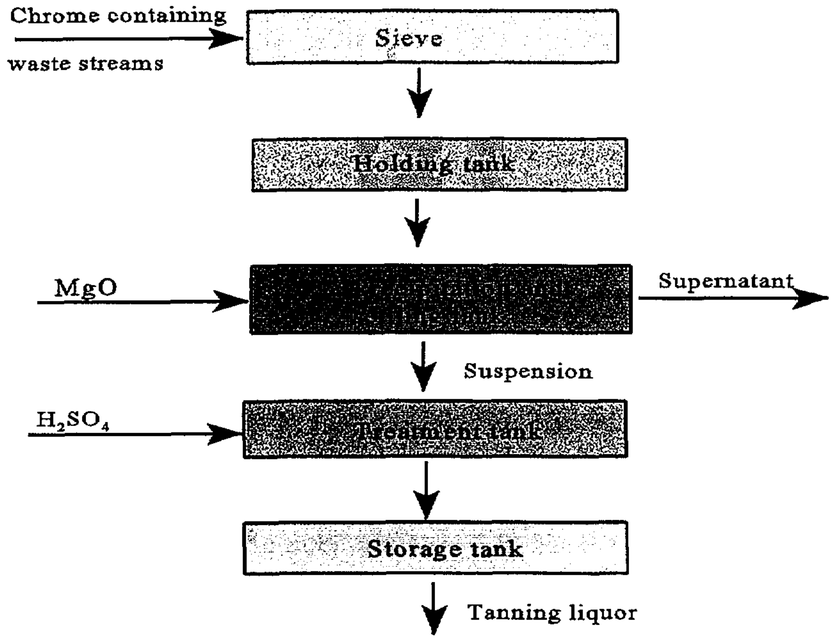
Figure 18
Flow Diagram of Chrome Recovery by Precipitation with Sodium Hydroxide/Carbonate



Option B

Slow precipitation with magnesium oxide, settling of the suspension, decantation of the supernatant and then acidifying the relatively dense precipitate. A simple flow diagram of this recovery system is shown in Figure 19.

Figure 19
Flow Diagram of Chrome Recovery by Precipitation with Magnesium Oxide



Any alkali precipitates chrome salts, but the stronger the alkali, the faster the rate of reaction and the slower the rate of coagulation.

The following general advice on the operation of a chrome recovery plant may be given:

- A preliminary screening is essential and, as required, fat removal by skimming.

- Alkali (sodium hydroxide or carbonate) should be added slowly, with stirring, as a hot, nearly saturated solution in an amount of 110-120 % related to the stoichiometric ratio. Polymer flocculant is dosed in a solution prepared according to instructions of the producer. The amount should be checked experimentally. In case of MgO, the chemical is added as a powder or pumped as a slurry to the collected floats under continuous stirring. However, the size and structure of MgO particles will influence the rate of reaction and settlement characteristics.

- The optimum condition for the precipitation is pH 8.5 - 9.0. Under standard conditions, normally, the pH value should not exceed 10.0 because a redissolving of chromium hydroxide occurs at a higher pH. In the case of the precipitation of floats from high fixing tanning, it can sometimes be useful to raise the pH over 10.0 and then to reduce it to 8.5 - 9.0. When using MgO, the pH value should be in the range 8.0 - 9.0, but overdosing will be less likely.

- A suitable temperature for the precipitation is 35 - 40°C. In the case of the precipitation of floats from a high exhaustion tanning, heating during the precipitation up to 60 - 80°C may be desirable. The greater the concentration of masking agents and other organics, the higher the temperature required.

- The precipitation usually takes up to 3 hours. When applying strong alkalies, a strongly hydrated chrome oxide sludge drops out and forms a suspension with very fine particles and long sedimentation/filtration time. Reduction of the high sludge volume is achieved with polymer flocculants. In the case of the precipitation with MgO, a hydrated chrome oxide sludge with a crystalline structure and short sedimentation/filtration time drops out. The value of the solubility product of chrome oxide hydrate is 2.9×10^{-29}, i.e. extremely low, so that the precipitate is practically insoluble in water.

- The hydrated chrome oxide sludge has to be settled by standing overnight or 24 hours and separated from the supernatant by decanting.

- The thickened suspension of chrome oxide hydrate is dewatered by a filter technique, typically by filter press. The filter cake should have min. 25 -30 % of dry substance.

- The filter cake is dissolved in concentrated sulphuric acid added in an amount of 2 kg per kg chrome oxide or more while stirring until pH 2.5 is reached. If necessary, additional heat should be supplied to raise the temperature of the mixture to nearly boiling. The redissolution depends greatly on the age and purity of the filter cake. The cake should be redissolved as soon as possible, as it becomes less soluble by standing. The tanning liquor is stored ready for reuse in a separate tank after adjusting its basicity. Mixing chrome hydroxide precipitate with dichromate, when in-house reduction is carried out, may be another way of achieving chrome reuse.

5.1.2. Recovery/Reuse Efficiency

The chrome oxide content in the recovered liquor is usually at a concentration of 100 - 150 g Cr_2O_3/l when conventional chrome tanning is applied. In case of recovering the chrome from high exhausted tanning floats, the chrome oxide concentration in the liquor will normally be lower.

A moderate concentration of organic compounds in the tanning liquors (fat, masking and high fixation auxiliaries, syntans) does not adversely affect the chrome precipitation and redissolving. Nevertheless, these compounds present in the recovered chrome liquor may sometimes cause problems in the production of high quality leather by inflicting a greyish tint on the leather and reducing the shade consistency.

It is recommended to pay attention to the fat content in recovered tanning floats. A fat concentration at less than 45 mg/l in the recovered chrome liquor should be observed in order to avoid discolouration of the leather. As far as polymer flocculants are concerned, they do not interfere with the reuse of the chrome liquor produced. Contaminants are decomposed by the hot sulphuric acid solubilisation step.

In general, note that some problems can arise in tanning if the chrome recovery is not done correctly. For example, the problem of staining is a consequence of the insufficient adstringency reduction of the reused spent float or the inadequate solubilisation of the chrome precipitate.

Practical Indian experience has shown (18) that leather tanned with 70 % fresh chrome and 30 % recovered chrome has more or less the same quality as leather tanned with 100 % fresh chrome.

In Germany, industrial trials have been carried out using various proportions of recovered chrome (19). If 50 % fresh chrome + 50 % recovered chrome was applied, some indications of an adverse effect on the leather quality were observed. Using 75 % recovered chrome, distinct differences were observed in the quality compared to the leather tanned only with fresh chrome. In view of the fact that only 25 - 30 % of the chrome offer is recoverable, one might not be afraid of adversely affecting the leather quality if the chrome recovery has been accomplished properly.

The tannery itself has to devise a technology of applying the recovered chrome liquor. If the tanning of grain leather is carried out with a powder tanning agent, the recovered chrome liquor can be used for split tanning. If the tanning is carried out with a fresh chrome liquor prepared by the reduction of dichromates, the recovered chrome liquor can be used as a partial replacement, maximum up to 30 % of fresh chrome.

When chrome shavings are hydrolyzed the resultant chrome sludge will normally be too contaminated with protein residues to be used for tanning. This fraction, however, can be used in dichromate reduction. Organic components will be oxidized by the dichromate and the chrome can be reused for tanning (7).

A model of the chrome distribution between leather and spent floats has been presented with respect to indirect chrome reuse by recovery (6). Corresponding data related to the chrome tanning/retanning efficiencies of 68 % and 90 % are presented in Table 7, Figures 20 and 21.

Table 7
Chrome Distribution between Leather and Spent Floats with Respect to Indirect Chrome Reuse by Recovery

	Distribution %			
	Efficiency 68 %		Efficiency 90 %	
Offer				
- total		100		100
- tanning	83		83	
- retanning	17		17	
Leather				
- total		68.3		90.0
- tanning	56.4		74.7	
- retanning	11.9		15.3	
Spent tanning float				
- recoverable	23.3		7.3	
- unrecoverable	1.5		0.5	
- total		24.8		7.8
Residual water recoverable				
- sammying	1.5		0.5	
- draining	0.3		0.1	
Spent retanning float				
- recoverable	4.2		1.3	
- unrecoverable	0.9		0.2	
Recovered				
- tanning	23.3		7.3	
- sammying/draining	1.8		0.6	
- retanning	4.2		1.3	
- total		29.3		9.2
Total				
- to reuse	**29.3**		**9.2**	
- to discharge	**2.4**		**0.7**	

Figure 20
Chrome Distribution Scheme
Indirect Chrome Reuse by Recovery
Tanning/Retanning Efficiency 68 %

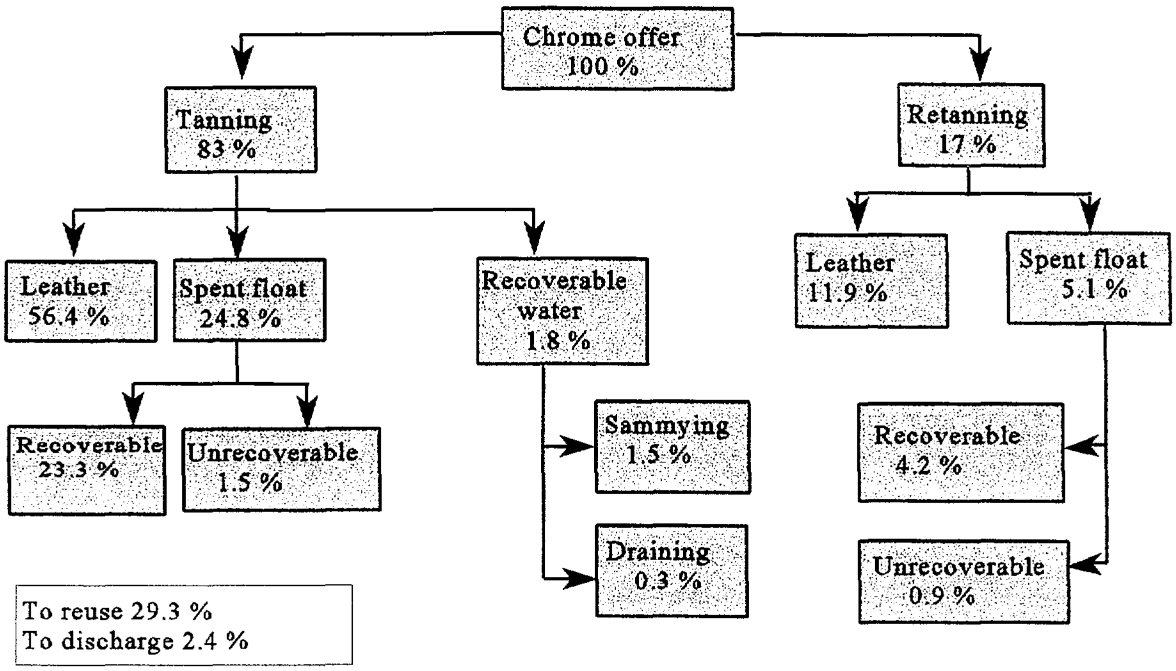
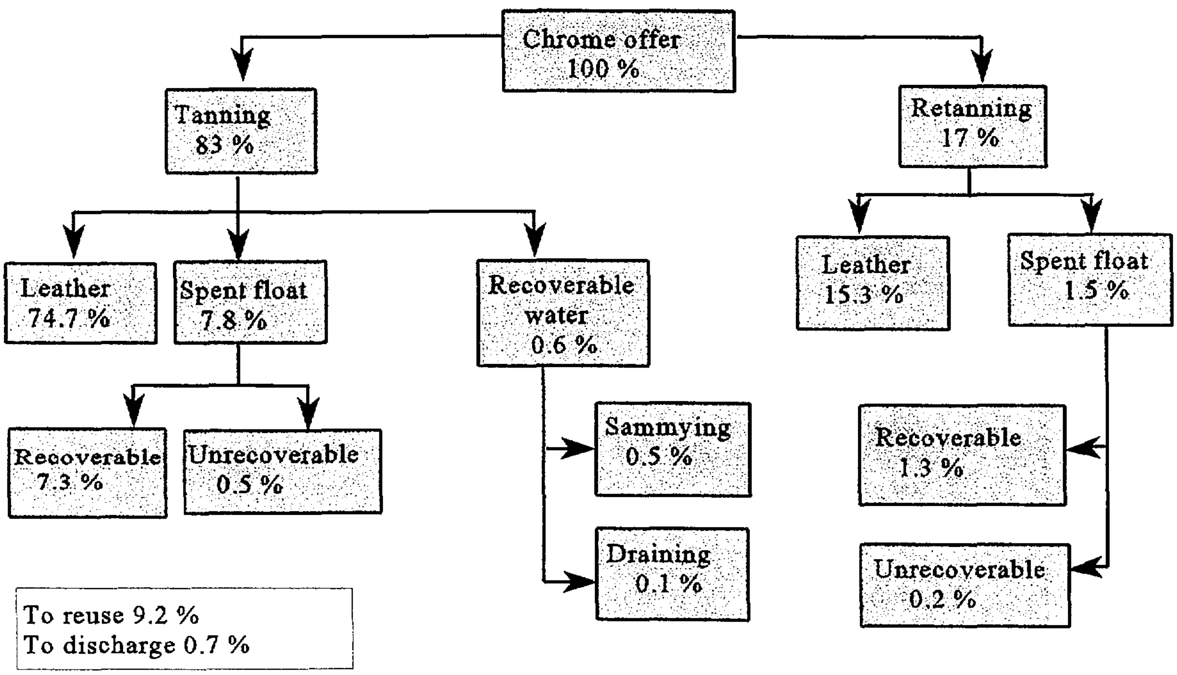


Figure 21
Chrome Distribution Scheme
Indirect Reuse by Recovery
Tanning/Retanning Efficiency 90 %



Some other models of the chrome distribution can be constructed as well. The model in Table 7, Figures 20 and 21 demonstrate one of several possible cases. It follows from this model that approximately 29 % of the chrome offer can be reused and saved by means of a recovery technique by precipitation when a conventional tanning is applied. Only 2.4 % of the chrome offer is discharged. In the case of a high exhaustion tanning, approximately 9 % of the chrome offer can be reused and saved while discharging only 0.7 %.

Considering the standard offer 2.0 % Cr_2O_3 on pelt weight, i.e. 2.2 % Cr_2O_3 on w/s weight, the effects of the chrome recovery/reuse related to a decrease of the chrome amount discharged in effluent are exemplified in Table 8.

Table 8
Influence of Chrome Recovery/Reuse upon Tanning/Retanning Efficiency and Chrome Amount Discharged in Effluent

	Tanning/Retanning	
	Conventional	High exhaustion
Efficiency %	97.6	99.2
Load discharge kg Cr/t w/s hides	0.36	0.12
Concentration in mixed effluent mg Cr/l		
- 30 m^3/t w/s hides	12	4
- 50 m^3/t w/s hides	7	-

It follows from Table 8 that chrome recovery/reuse, if correctly performed, lowers the chrome load discharged in effluents to 0.12 - 0.36 kg Cr/t w/s hides. Then the chrome concentration in the effluent occurs in a range of 4 - 12 mg Cr/l. Residues of unrecovered spent floats, leather fibres, namely buffing dust, the supernatant and/or filtrate with a chrome amount 1 - 10 mg/l, are sources of the residual chrome concentration in effluent. To reduce this concentration close to a value of 1 mg Cr/l, residual floats from washing, neutralization and fatliquoring must be precipitated too.

5.2. Recovery without Reuse

To eliminate the chrome from residual floats to the highest degree, all chrome containing wastewater from post tanning operations in the mixture with tanning wastewater have to be precipitated. Organic substances in residual floats from neutralization, retanning, fatliquoring and dyeing mean that the chrome precipitated cannot be reused.

Calcium hydroxide is considered to be the most frequently used precipitant. To fully accomplish the chrome precipitation, ferric and/or aluminium salt is added with the lime. To reduce the volume of the precipitate, an organic polyelectrolyte should be added prior to settling and filtering.

The recent EC research project "Reduction of Chromium Discharge from the Leather Industry" (20) has focused inter alia on the precipitation of spent post tanning floats in order to achieve the concentration of 1 mg Cr/l in chrome containing waste streams. Selected results of large scale trials are summarized in Table 9.

Table 9
Precipitation of Combined Wastewater from Tanning and Post Tanning Operations with Lime and Ferric Chloride

Wastewater	Concentration mg Cr/l	
	Inlet	Outlet
Conventional tanning:		
- mixed wastewater 1	321	0.38
- mixed wastewater 2	460	1.26
High fixation tanning		
- mixed wastewater	27	0.36

The results substantiate that the chrome can be almost totally recovered by precipitation with lime and ferric chloride. The concentration of 1 mg Cr/l is attainable. Assuming a water consumption of 30 m^3/t w/s hides, the residual chrome load discharged in effluent will be 0.03 kg Cr/t w/s hides. Chrome containing sludge is not reusable and must be deposited in special landfill sites.

6. COST RATIOS

The extent of the chrome management implementation depends on the required chrome concentration and/or chrome load discharged in effluent. The tanner has to apply whatever measures are necessary to meet the local chrome regulations. The tanner is interested in corresponding technical and operational measures, and chrome tanning procedures that are reasonable with respect to costs but do not affect the commercial value of the leather and its properties. The tanner's effort is aimed at saving the chrome by its higher utilization and reducing chrome losses in processing.

Costs associated with improving chrome management should be related to the particular conditions of the given tannery. Notwithstanding, it is reasonable to give a general example of chemical cost ratio between two modifications of high exhaustion chrome tanning and conventional tanning. Corresponding data are given in Table 10.

Table 10
Operational Chemicals Cost of High Exhaustion Tanning Compared to Conventional Tanning (Chrome Offer 2.0 % Cr_2O_3).

Modification A - **High Exhaustion Procedure with Self Basifying and Organically Masked Chrome Tanning**

Modification B - **High Exhaustion/High Fixing Procedure with Self Basifying/Organically Masked Chrome Tanning and Glyoxylic Acid in Pickling**

Operation	Chemical cost US$/t pelt weight		
	Conventional tanning	High exhaustion tanning	
		Modification A	Modification B
Pickling	14.2	11.1	46.7
Tanning	83.7	106.5	86.5
Total	97.9	117.6	133.2

It follows from Table 10 that, the implementation of a high exhaustion tanning procedure, will increase the operational cost of chemicals by 20 - 36 % to meet regulations on the chrome amount allowable in effluent. On the other hand, however, about 30 % of the chrome offered in the tannage will be saved.

An example of cost ratio of chrome recovery can also be mentioned. Chrome recovery/reuse offers not only an important environmental benefit but there is a cost saving in fresh chrome and effluent treatment as well. The cost effectiveness depends on the efficiency of collecting the floats, treatment efficiency, capital and running cost.

The chrome recovery technique affects capital and running costs. The choice between an alkali sodium salt and MgO is decisive for the level of capital costs since as a rule a filter press is not necessary for dewatering the chrome oxide precipitated with MgO. For a daily chrome recovery capacity of 12 - 15m^3 spent floats, capital costs should be expected as follows:

Chrome recovery with alkali sodium salt precipitation: 150,000 - 200,000 US $

Chrome recovery with magnesium oxide precipitation: 60,000 - 80,000 US $

As regards the running costs, annual operating costs of an Indian chrome recovery plant are available (18). Corresponding data are summed up in Table 11.

Table 11
Annual Operating Costs of a Chrome Recovery Plant
Basic indications: processing capacity 3,000 t/year
recovery capacity 9 m^3/day of spent floats
precipitation with MgO, no mechanical dewatering

Item	Cost/US$
Maintenance	1,500
Labour	1,000
Chemicals	9,000
Electricity	500
Miscellaneous	2,000
Total operating costs	14,000
Financial costs	7,800
Depreciation	5,200
Total annual costs	27,000

It is obvious from Table 11 that chemicals (MgO, sulphuric acid) share significantly (60%) in operating costs. Prices of the precipitants are dependent on where they are produced. Typical European prices are as follows:

MgO	1.07 US$/kg
Na_2CO_3	0.83 US$/kg
NaOH	0.29 US$/kg

Evidently the cost of chemicals will be higher when spent floats are precipitated with MgO. It follows from data of an Indian chrome recovery plant that total annual costs related to processed hides amount to 9 US$/t raw hides. Taking into consideration operating costs of mechanical dewatering, the total annual costs related to one tonne of processed hides will be higher in the majority of cases when mechanical dewatering is applied.

Figure 22
Payback Time as a Function of Recovery Plant Capacity

Operational experience has made it possible to calculate the profitability of chrome recovery plant based on using MgO (14, 21).The profitability expressed in terms of the payback time is shown in Figure 22.

Considering a reasonable payback time is 3 years, the chrome recovery plant based on using MgO would be profitable at a capacity as low as 2.5 m^3/day. It may be calculated with a longer payback time in the case of a recovery plant based on using alkali sodium salt and mechanical dewatering as well. Generally, the higher the recovery plant capacity, the better should be the profitability.

The profitability level is influenced by the total volume of spent floats recovered. In the case of conventional chrome tanning, up to 30 % of the chrome offer contained in spent floats can be recovered. In addition, the profitability may also be assisted by reuse of supernatant water or filtrate as a float in first soaking or pickling.

The choice between direct float recycling or indirect recovery depends on individual circumstances in the tannery concerned. With regard to a direct recycling technique the following circumstances should be especially mentioned :

- Lower capital costs (sieve, storage tanks, pumps, distribution pipes)
- No additional chemicals
- Lower running cost
- Excess floats volume
- Lower chrome reuse in practice

From the economical point of view, in general, there is no explicit recommendation to the optimum mode of reusing the chrome from spent tanning/retanning floats.

7. ADVANTAGES AND LIMITATIONS OF VARIOUS METHODS

Substantially increased chrome utilization in tanning operations is a basis of high level chrome management. There are three methods to increase the chrome utilization, i.e. high exhaustion chrome tanning, direct recycling of spent floats and chrome recovery/reuse. The efficiency of individual options is described in previous sections. Circumstances needed to minimize the chrome load in effluent have been evaluated. To help tanners in the choice of a suitable option, features of individual options are summarized.

Advantages and limitations of a high exhaustion chrome tanning are summed up in Figure 23.

Figure 23
Advantages and Limitations of High Exhaustion Chrome Tanning

Advantages	Limitations
Savings in chrome used	Deliming should be as complete as possible
Reduced level of chrome in waste streams	Longer running time needed
Reduced level of sulphates in waste streams	Higher temperature required
Reduced level of water consumption	Slip agent needed to avoid abrasion of grain
High chrome fixing, leaching minimized	Improved drum drive system required
Sammying immediately after leather unloading	Increased level of process control needed
Flexible, applicable to any type of leather	Higher running costs
No loss in leather quality	

Advantages and limitations of a chrome tanning with float recycling are summed up in Figure 24.

Figure 24

Advantages and Limitations of Chrome Tanning with Float Recycling

Advantages	**Limitations**
Savings in chrome used	Build up of excess liquor volume
Reduced level of chrome in waste streams	Mechanical pretreatment of waste streams required
Reduced level of neutral salts in waste streams	Some change to tanning procedures needed
Reduced level of water consumption	Increased level of process control needed
No additional chemicals needed	Some differences in leather colour possible
Simplest form of reuse	Some capital costs needed
Can be operated indefinitely	Slightly increased running costs
Flexible, applicable to any type of leather	
No loss in leather quality	

Advantages and limitations of a chrome tanning with chrome recovery/reuse are summed up in Figure 25.

Figure 25
Advantages and Limitations of Chrome Tanning with Chrome Recovery/Reuse

Advantages	Limitations
Savings in chrome used	Mechanical pretreatment of waste streams required
Reduced level of chrome in waste streams	Increased discharge of neutral salts
Close to using fresh chrome	Additional chemicals and man power required
Minimum procedure change in tanning	Increased level of process control needed
Treating all liquors	More complex plant needed
No build up of excess liquor volume	Some differences in leather colour possible
Can be operated indefinitely	Higher capital costs
Flexible, applicalbe to any type of leather	Higher running costs
No loss in leather quality	

8. CONCLUSIONS

Management of the chrome tanning process and chrome wastes in a tannery are primary concerns in a successful operation. The material balance in leather manufacture has proved that in the traditonal process less than 50 % of the chrome input is found in leather while more than 50 % is disposed in solid/liquid waste streams.

For this reason, chrome management aims to improve the chrome utilization in tanning processes as high as possible in order to minimize the amount of chrome discharged into effluent. Under normal conditions only 60 - 80 % of the chrome offer is utilized in tanning. In general, leather manufacture produces a chrome discharge of 3 - 7 kg Cr/t w/s hides, which corresponds to a concentration of 60 - 140 mg Cr/l in mixed wastewater streams for a water consumption of 50 m^3/t w/s hides. This concentration is not acceptable according to current legislative limits in many countries.

There are three principal approaches found in practice to attain high chrome utilization in tanning processes, namely high chrome uptake in tanning, direct tanning floats recycling, and chrome recovery/reuse after its precipitation and redissolving.

An optimization of process parameters and tanning process modifications are two effective ways of increasing the chrome uptake in tanning. Mechanical action, chrome concentration, chrome offer, pH, temperature and reaction time are the main parameters to be optimized.

Better chrome uptake can be achieved by finishing the tanning at the highest possible pH and temperature. End values up to 40 - 45°C and pH 4.0 - 4.2 are advantageous. Benefits will be obtained by using the least amount of chrome offer combined with a tanning time as long as possible and fast running. A chrome offer lower than 1.7 % Cr_2O_3 on pelt weight is not recommended without modifying the tanning process. It is stated that the chrome amount discharged from the tanning operation fluctuates in a range of 2 - 5 kg Cr/t w/s hides. When optimizing process parameters in order to increase the chrome uptake, the amount of chrome discharged in effluent occurs at the lower end of the range.

Tanning process modifications may involve masking the chrome tanning complexes and increasing the collagen reactivity. The combination of process modifications and the optimization of process parameters are the basis of modern high exhaustion chrome tanning processes. The chrome utilization in a high exhaustion tanning can be increased up to 98 %. The chrome offer can be reduced from a standard level 2.0 % Cr_2O_3 down to 1.3 % Cr_2O_3 on pelt weight depending on the pelt thickness, without affecting the leather quality. Chrome leaching in post tanning operations can be minimized as well. An improved drum drive system and an increased level of process control are required. High exhaustion tanning can result in discharging only 0.4 kg Cr/t w/s hides. A concentration of 13 mg Cr/l may be expected in mixed waste water streams when assuming a water consumption maximum 30 m^3/t w/s hides in a modern tannery.

Recycling of spent floats from the chrome tanning directly back into processing is the simplest way of chrome reuse. Several recycling techniques are industrially employed. By means of a simple recycling technique, 90 % efficiency is attainable. The efficiency is limited by a build up of the excess liquor volume. Better float collection and more sophisticated recycling technique facilitates attaining of 95 - 98 % efficiency. Then the chrome amount discharged in effluent will be decreased to 0.30-0.75 kg Cr/t w/s hides. Increased level of process control and some capital costs are required.

Chrome recovery is an indirect way of recycling the chrome in leather production. This enables the tanner to avoid a problem of accumulating float volume. The principle consists of recovering the chrome from residual chrome containing floats by precipitation, the separation of suspension, and then redissolving it in the acid for reuse. Variations arise in the base used to precipitate the chrome (sodium hydroxide/carbonate, magnesium oxide) and in the need of applying a filtration technique. Higher capital and running costs are to be expected.

The choice among a high exhaustion tanning, direct floats recycling and indirect recovery/reuse depends on individual conditions in the tannery concerned. There is no explicit recommendation to the optimum way of reusing the chrome and reducing it to the lowest level in the wastewater stream.

A summarized survey of the chrome balance shows that 40-45 % of the chrome offer remains in the leather, 26-30 % in the solid waste and about 30 % in effluent when processing the leather by conventional tanning and/or chrome retanning with the chrome offer of 15-17 kg Cr/t w/s hides. A share of 21-24 % of the chrome offer can be recovered and reused. Processing the leather by high exhaustion tanning and/or chrome retanning with the chrome offer 10-13 kg Cr/t w/s hides, a share of 57-60 % of the chrome offer remains in the leather, 32-38 % in the solid waste and 3-8 % in effluent. Only a share of 1-5 % of the chrome offer can be recovered and reused.

The lowest chrome amount practically attainable in effluent in somewhere between 0.3 - 0.4 kg Cr/t w/s hides. Then in case of a standard effluent production of 30 m^3/t w/s hides, the chrome concentration ranges within 10-14 mg Cr/l. However, legislative requirements are most frequently in the range of 1-4 mg Cr/l. In that case it is inevitable to precipitate all waste streams from tanning/post tanning operations after recovering the chrome. Calcium hydroxide in a combination with ferric and/or aluminium salt are considered to be the most suitable precipitants. Only after precipitation a concentration of about 1 mg Cr/l corresponding to the amount of 0.03 kg Cr/t w/s hides is attainable.

REFERENCES

1. Bosnic, M., Buljan, J., Daniels, R. P.: Pollutants in Tannery Effluents. UNIDO, Vienna, 1998.
2. Poncet, T: Sludge Landfill Model Site Manual. UNIDO, Vienna, 1998.
3. Environment Commission of I.U.L.T.C.S.: IUE Recommendations for Solid By-Product Management. London 1997.
4. Buljan, J., Reich, G., Ludvik, J.: Mass Balance in Leather Processing. UNIDO, Vienna, 1997.
5. Environment Commission of I.U.L.T.C.S.: IUE Recommendations on Cleaner Technologies for Leather Production. London 1997.
6. Covington, A. D.: Chrome Management. Proceedings of the Workshop on Pollution Abatement and Waste Management in the Tanning Industry. Ljubljana, 1995.
7. Frendrup, W.: UNEP Cleaner Production Industrial Sector Guide. Leather Industry. Taastrup, 1995.
8. Heidemann, E.: Fundamentals of Leather Manufacturing. Darmstadt, 1993.
9. Covington, A. D.: JALCA 86, 376 (1991).
10. Covington, A. D.: JALCA 86, 456, (1991).
11. Daniels, R. P.: World Leather 7, No.2, p.73 (1994).
12. Fuchs, K. H., Kupfer, R., Mitchell, J. W.: JALCA 88, 402, (1993).
13. Bayer, AG.: Tanning, Dyeing, Finishing. Leverkusen, 1987.
14. van Vliet, M.: Cleaner Technologies. Proceedings of the Workshop on Topical Questions of the Environment Protection in the Leather Manufacturing. Partizánske, 1996.
15. Francke, H.: Das Leder 44, 89 (1993).
16. Ludvik, J.: Scope for Decreasing the Pollution Load in Leather Processing. UNIDO, Vienna, 1998.
17. Davis, M. H., Scroggie, J. G.: JSLTC 57, 13, 35, 53, 81,173 (1973).
18. Rajamani, S.: Appropriate Chrome Recovery and Reuse System - Experience in Indian Tanneries. Proceedings of the Workshop on Pollution Abatement and Waste Management in the Tanning Industry. Ljubljana, 1995.
19. Hellinger, K.: Chrom-Rückgewinnung und Eliminierung bei der Lederherstellung. 1. Freiberger Polymertag. Freiberg, 1993.
20. Rydin, S.: Reduction of Chrome Discharge from the Leather Industry. Minutes of the European Workshop on Environmental Technologies in the Leather Industry. Bologna, 1995.
21. van Vliet, M.: World Leather 7, No.6, p.15 (1994).

ANNEX 1

Standards for land-application of Cr-containing sludge (Compilation of different legislations)

Parameter	**Denmark**	**France**	**Germany**	**The Netherlands**	**Belgium**	**Norway**	**Sweden**	**Switzerland**	**United Kingdom**	**USA**
Maximum acceptable concentration in the soil *mg Cr/kg of dry soil*	100	150	100	100[1]	150				600	No limit (3,000 before 1993
Maximum concentration in sludge *mg Cr/kg of dry sludge*	100	1,000	900	500	500	200	150	1,000		No limit (150 before 1993)
Suggested annual chrome loading *(kg/ha/yr)*		6.0	2.0	1.0	2.0	0.4	1.0	2.5		No limit (3,000 before 1993)
Maximum recommended chrome loading *(kg/ha)*		360	210	100		4			1,000	
Suggested maximum annual sludge solids application *(t/ha/year)*	1.5	3.0	1.7	2 (arable) 1 (grass)		2	1	2.5		
Maximum sludge solids loading *(t/ha)*			167	200		20	5 in 5 years			
Minimal soil pH		6.0							6.5 (arable) 6.0 (grass)	

[1] Varies according to clay content