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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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

CHROME MANAGEMENT IN THE TANYARD

Prepared by

J. Ludvík
UNIDO Consultant in Leather Pollution Control

Project Manager

J. Buljan, Agro-Industries and Sectoral Support Branch

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1. INTRODUCTION

Chrome tanning is the most common type of tanning in the world. Chrome tanned leathers are characterised by top handling quality, high hydro-thermal stability, user-specific properties and versatile applicability. Waste chrome from leather manufacturing, however, poses a significant disposal problem.

Waste chrome is contained in:

- Liquid waste: Spent floats from tanning and re-tanning, as well as waste from sammying and draining.
- Sludge: Dewatered slurry resulting from sedimentation of suspended solids during primary (physico-chemical) effluent treatment.
- Tanned (solid) waste: Shavings, buffing dust and unusable (mostly wet blue) split, as well as crust and finished leather trimmings.

Throughout the world, chrome discharge from tanneries is subject to strict regulations. That notwithstanding, chrome is a component that has to be strictly monitored.

The environmental impact of chrome discharged from tanneries has been a subject of extensive scientific and technical dispute. Although the legislative limits on the disposal of solid chrome-containing waste have been relaxed in some countries, liquid emissions remain strictly regulated throughout the world.

Limits on total chrome discharge in effluent vary widely between 0.05 and 10 mg/l for discharges into water bodies (direct discharge) and 1-50 mg/l on discharges into sewage systems (indirect discharge) (1).

Chrome-containing sludge is mostly disposed of in landfill which have to be provided with a leachate collection and treatment system. The use of sludge in land applications is governed by very strict regulations in most European countries (2). Monitoring focuses on such typical parameters as: initial chrome concentration in the soil (mg Cr/kg dry soil); Cr content in the sludge (mg Cr/kg of dry sludge); and cumulative (maximum) chrome load over a 10 year-period (kg Cr/hectare). Specific values for European countries and the United States of America are presented in Annex 1.1

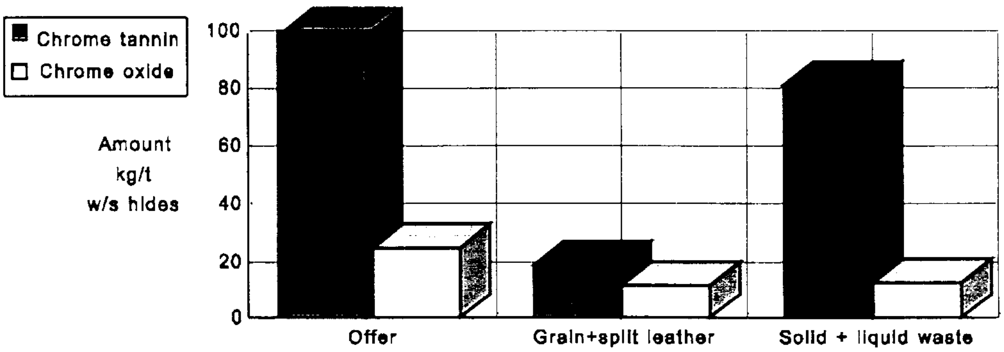
Some tanned wastes are partly used in by-products, but most are deposited in landfill. Blue shavings and trimmings are used in the manufacture of leatherboard; they also undergo chemical and/or enzymatic hydrolysis, pyrolysis, and incineration (3). Recently, however, possibly owing to improved analytical methods and growing concern about protecting the environment, the presence of potentially harmful hexavalent chromium in leather has been detected.

Given the close link between chrome tanning and the environmental impact of leather manufacturing, chrome management is of primary importance in tanning operations. This paper provides updated information on chrome management and those techniques most frequently used to reduce the amount of chrome in tannery wastewater. By providing updated information and citing practical experience, the paper aims at contributing to an expansion of leather manufacture without harming the environment unnecessarily.

2. CONCERNS OF CHROME MANAGEMENT

A tanner's primary concern in chrome management is the balance or ratio between the amount of chrome remaining in grain leather and split, and the amount retained in the solid waste, and the amount discharged in effluent. A typical balance for conventional tanning is shown in Figure 1.

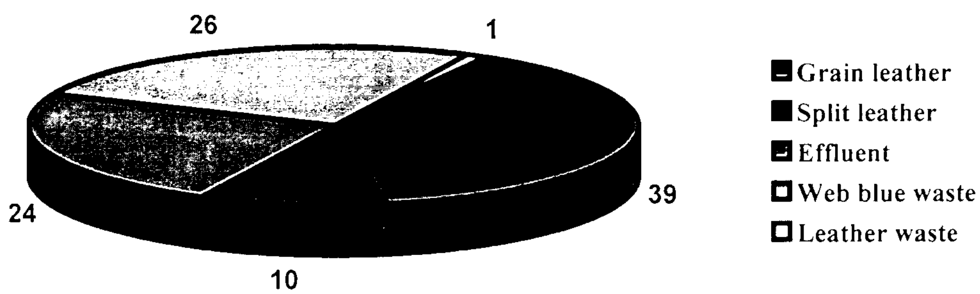
Figure 1
Chrome balance in leather manufacture according to (4)



The balance is based on a general application of chrome tannin containing 25 % Cr_2O_3 and neutral salts. It is calculated for the use of: (a) 2 % Cr_2O_3 on pelt weight for tanning; and (b) 1.2 % Cr_2O_3 on shaved weight for re-tanning. In these models, it is also assumed that chrome reacts with pelt collagen in the form of basic chrome sulphate.

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, percentage



2.1. Chrome management in tanning processes

Pickling, tanning, sammying, draining and post-tanning are crucial operations in chrome management. The amount of chrome discharged in effluent in the course of processing one tonne of wet salted hides may be summarised 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

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

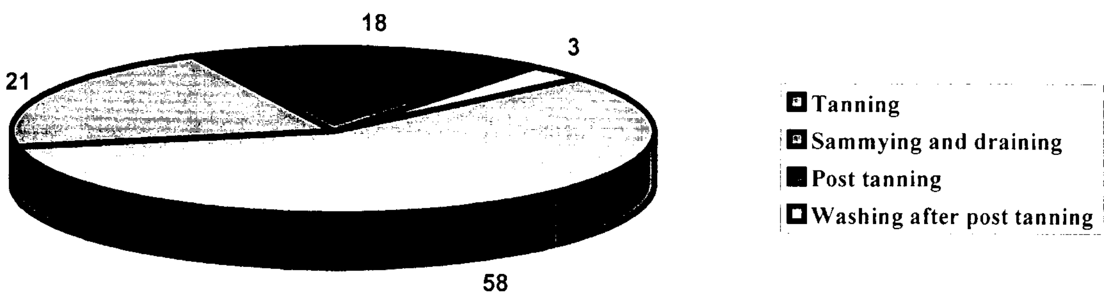
Table 1
Chrome discharged in effluent from individual operations

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 shown above is repeatedly found in practice. In general, chrome uptake under typical technological conditions is of the order of60 - 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 confirm that while the main portion of the chrome discharged comes from the tanning float, significant amounts are discharged from sammying and re-tanning. Chrome management must thus focus on all operations in the tanyard and the wet finishing department; maximising chrome uptake should be the first priority in any chrome management improvement project.

Quite recently, thought was given to the idea of replacing the chrome by another metal. Regrettably, practical experience to date, however, shows that no metal tanning agent matches the versatility of chrome (III). Total chrome replacement is possible if reduced hydro-thermal stability and lower handling qualities are acceptable. However, most end-uses of leather require high hydro-thermal 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 considered 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 stabilised structure can be split (should this not have been done after liming), shaved and trimmed. After mechanical processing, the main chrome tanning stage ensues, in the course of which only some 9.5 kg Cr_2O_3/t wet salted (w/s) hides are needed in comparison to the conventional volume of 21 kg Cr_2O_3/t (7). The primary advantage is one of economising on the use of chrome and minimising the production of chrome tanned waste. That notwithstanding, for a variety of reasons (including difficulties assocaieted with shaving) wet white technology has found limited practical use hitherto and its commercial acceptance is low.

2.2. Waste chrome management

The management of waste chrome is not a matter to be neglected either. The amount discharged under standard technological conditions, 3 - 7 kg Cr/t w/s hides, represents a concentration of 60 - 140 mg Cr/l in mixed wastewater streams within a total water consumption of 50 m3/t w/s hides. This concentration is not acceptable in many countries given the legislative limits on direct/indirect effluent discharge and sludge landfilling. Thus, every chrome management project has to address the problem of reducing the chrome concentration in effluent not only by maximising chrome exhaustion in tanning, but also by applying supplementary methods, such as recycling chrome-tanning floats and chrome recovery/reuse.

3. IMPROVING THE CHROME TANNING PROCESS

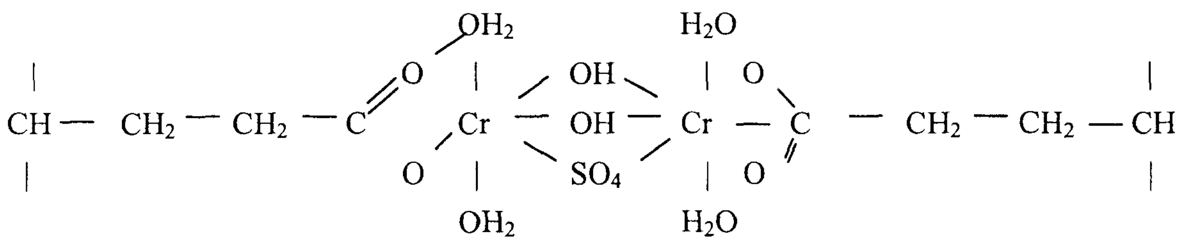
The standard chrome tanning process can be roughly divided into three phases: pickling, tanning and basification. Previously these phases were kept strictly separate and were carried out in sequence, whereas today they often overlap.

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 uses 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. Sodium chloride, NaCl, is generally used for this purpose. Under standard conditions, 40 - 60 % float on pelt weight is applied, the pickling time being 1-2 hours and the float pH 2.8 - 3.0.

Tanning

Reaction sites for chrome tanning are the ionised carboxyl groups on side chains of the collagen. The lateral cross-linking of chrome complexes was suggested, e.g.



In this structure the chrome complexes are bound to 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 are used in powder form; they contain about 25 % Cr_2O_3 of 33 % basicity. Basic chrome sulphate liquors are also used. These liquors are prepared by reducing the Na/K dichromates in the presence of sulphuric acid. As a rule, reduction is carried out using 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 ensues during the tanning operation in order to neutralise pickling acids and any acid produced in reaction with the collagen. At the same time, the reactivity of chrome complexes is enhanced on account of their basicity; it increases steadily from 33 % up to 66 % at the end of the tanning process.

Sodium hydrogen carbonate is often used as a basification agent. Usually the dosage is given towards the end of the tanning process in several portions in a total amount of 0.8 - 1.2 % on pelt weight in order to achieve a final pH 3.8 - 4.2 in the float. Magnesia, usually containing 60 % MgO, may also be used as a self basifying agent. Owing to its low solubility, the latter 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 to 3.8 - 4.2. Chrome tannins containing a self basifying component based on MgO or dolomite are also commercially available. 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°C. The drumming time should be at least 6 - 8 hours. As a rule, the chrome concentration in spent float is in a range of 3.5 - 7.0 g Cr_2O_3/l. After drumming, the leather is unloaded, drained and sammed.

In order to improve the chrome tanning process, it is essential that the chrome uptake be increased so as to reduce the chrome concentration in residual floats to a maximum degree. Two main approaches to increasing the chrome uptake during the tanning process are adopted:

- Optimising the process parameters-
- Modifying the tanning process

Both approaches offer various options of increasing the process efficiency.

3.1. Optimising the process parameters

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

3.1.1. Mechanical action

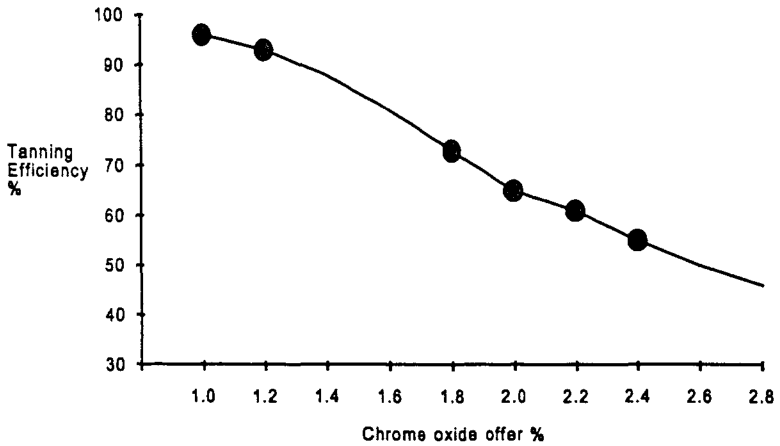
Mechanical action, agitation in the drum, is the prime means of transporting chemicals into the substrate. In the case of chrome tannins, intensive agitation is indispensable to achieving good chrome penetration and securing the time needed to complete the reaction of the whole system. The intensity of agitation is primarily governed by the drum dimensions and speed. In practical terms, optimum mechanical action is given when the drum speed is some 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, in turn, is a decisive factor in diffusion. The higher the chrome concentration in the float, the faster the chrome penetration into the fibre structure. Similarly, the lower the concentration, the slower the rate of the reaction between collagen and chrome. Good penetration is a precondition for the final through-reaction in all layers of the pelt. All tanning recipes address this fact and prescribe a certain excess offer of tannin agent for reasons of safety and quality. However, this always causes problems with the chrome and other chemicals remaining in spent floats.

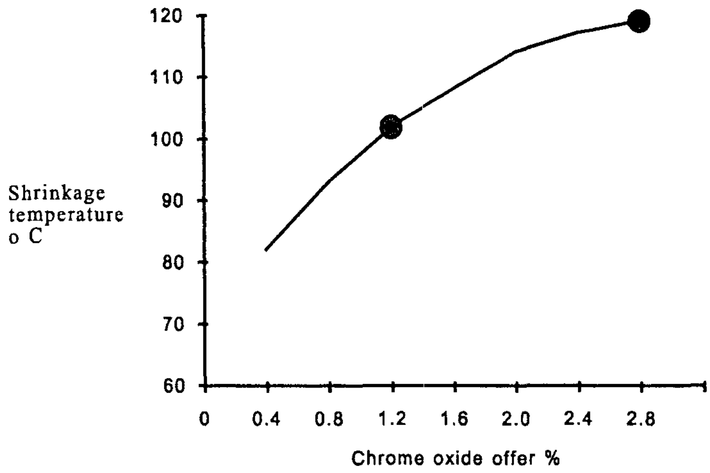
In the form of a binuclear basic chrome sulphate, chrome reacts quite specifically with ionised carboxyl groups of the collagen. The efficiency of chrome tanning, defined as a proportion of the chrome offer fixed to the collagen, is illustrated in Figure 4.

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)

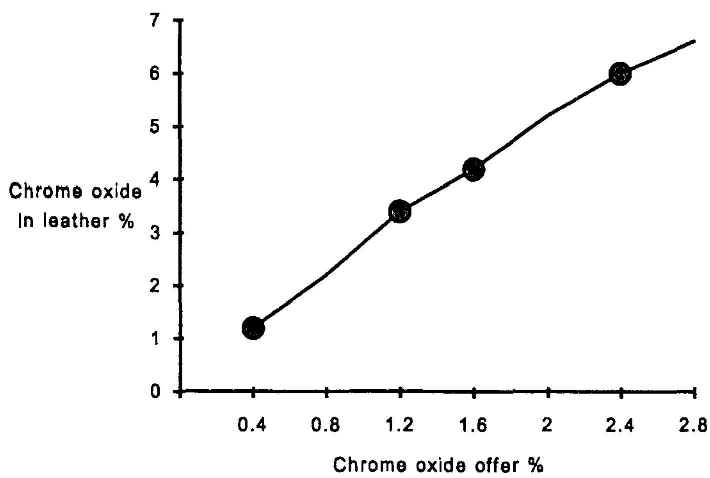


Approximately 2% Cr_2O_3 is sufficient to achieve a shrinkage temperature of 110°C or more; this affects the boil fastness of leather. Increasing the chrome offer further yields no practical benefit. With an offer of 2 % Cr_2O_3, chrome tanning reaches an efficiency of only 65 % (see Figure 4) , whereas in practice efficiencies of 60-80 % can be achieved with less.

A shrinkage temperature of 100°C can actually be reached with an offer of about 1 % Cr_2O_3. However, under normal conditions, applying a chrome offer of less than 1.6 - 1.7 % Cr_2O_3 may make it difficult to achieve boil fastness and obtain a uniform cross-sectional distribution of chrome throughout the leather (8).

If the chrome offer increases, the chrome content in leather will also increase, 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 a shrinkage temperature of 100oC (8).

For quality reasons, when applying a standard tanning procedure, the tanner has to take care to minimise the chrome offer and reduce the chrome concentration in effluent. When aiming to reduce the chrome concentration in effluent without impairing leather performance and quality, the tanner should make every effort to optimise other process parameters and/or modify the tanning process.

3.1.3. Reaction time, pH and temperature

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

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

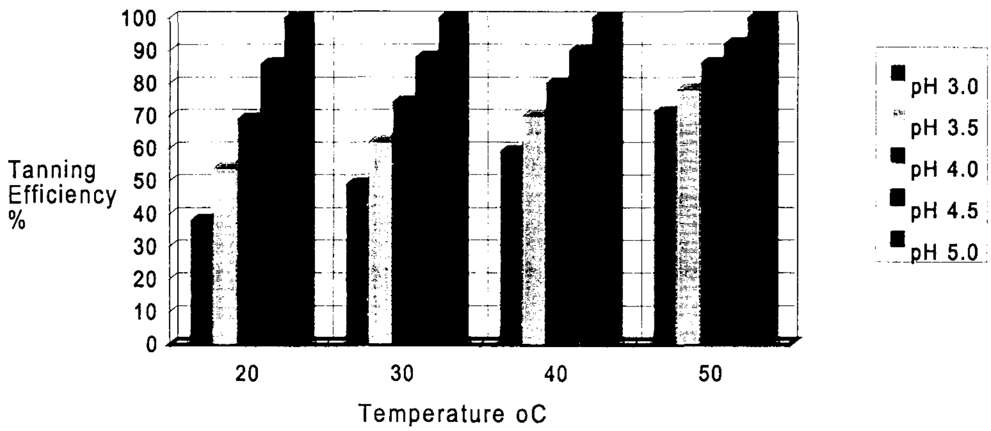
It is important to recognise the difference between pH and temperature in terms of their impact on chrome fixation and the corresponding shrinkage temperature. Increasing either the temperature or the pH of chrome tannage will always increase chrome fixation. It is also generally true that increasing the chrome content of a leather will increase the shrinkage temperature. However, it should be remembered that increasing the temperature primarily governs chrome fixation, whereas increasing pH primarily governs the rise in shrinkage temperature.

Furthermore, the relationship between chrome uptake and shrinkage temperature depends on the manner in which the tanning reaction is conducted: more specifically, the timetable for temperature and pH rise during tannage.

- The earlier the heating is started, the higher the chrome uptake will be. In other words, the later the heating is applied, the lower the chrome uptake will be.
- The heating timetable has little or no effect on the shrinkage temperature ultimately achieved. Conversely, the basification timetable has little or no effect on the chrome uptake.
- Early basification is likely to yield 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 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 levels. The problem is that of maintaining the reaction between the chrome complex and collagen and avoiding chrome precipitation. An example of changes in tanning efficiency in relation to the final float pH and temperature is given in Figure 7. The results are taken from a series of graphs which indicate 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 careful basification, it is possible to basify to pH 5.0 without causing chrome staining and so achieve the highest chrome uptake. However, for commercial applications, such a procedure should not be recommended unless very strict process monitoring and control systems are in place.

Given the leather quality requirements and the need to decrease the chrome concentration in effluent, the factors to be optimised in the chrome tanning process are summarised in Figure 8 below which is based on a survey conducted by (6).

Figure 8
Factors to be optimised in the chrome tanning process

Reduce
Chrome offer
Pace of pH and temperature changes

Increase
Mechanical action
Temperature
pH
Reaction time

Many years of experience have shown that:

- 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 of up to 40 - 45°C and pH 4.0 - 4.2 are advantageous.
- Benefits are obtained by using the least amount of chrome offer combined with a high chrome concentration in the float, extending the tanning time as far as possible and using high drum speeds. A chrome offer lower than 1.7 % Cr_2O_3 is not recommended for commercial applications.

3.2. Modifying the tanning process

For the most part, modifications designed to improve chrome uptake and reduce chrome concentration in effluent involve masking the chrome tanning complex and increasing the collagen reactivity. All such modifications are usually combined with an optimisation of the tanning process parameters. A combination of process modifications and the optimisation of process parameters constitutes the basis for a modern, environment friendly high-exhaustion chrome tanning process.

3.2.1. Masking in chrome tanning

Masking is defined as the 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 permit 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 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 cross-link two chromium (III) molecular ions; this makes the chrome species bigger, thus increasing the reaction rate but decreasing the penetration rate. By including an organic acid, the complexes are less cationic, thus reducing the astringency or affinity to the collagen. The masked chromium salt penetrates the substance more easily and chrome distribution over the cross-section is more uniform. Today masked chrome tannins are commercially available. Tanning liquors with a low degree of masking are produced when acid dichromate is reduced with molasses.

Several other tanning auxiliaries are available on 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 the tanning process 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 basification (6). A more recent development is to increase the complexity of poorly bound or unbound chrome by applying low molecular weight polyacrylates during tanning or re-tanning (8).

3.2.2. Increasing collagen reactivity

The main way of increasing collagen reactivity is to increase the number of carboxyl groups on the amino acid side chains in order to provide more sites for crosslinking. To this end, glyoxylic acid was suggested as a means of condensing additional carboxyl groups into the collagen, using the Mannich reaction (12).

Glyoxylic acid has been found to facilitate tanning when used in the pickle prior to 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 thus exhausted more effectively and fixed more firmly than in conventional tanning. Tanning auxiliaries based on glyoxylic acid are also commercially available.

3.2.3. Efficiency of high-exhaustion tanning

Illustrated below are some examples of high-exhaustion tanning procedures and their effects on reducing chrome content 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.

The results of a high-exhaustion tanning process according to Example 1 above compared to a conventional chrome tanning can be seen in Table 2.

Table 2
Chrome concentration in residual floats from high-exhaustion and conventional tanning process according to (13)

	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

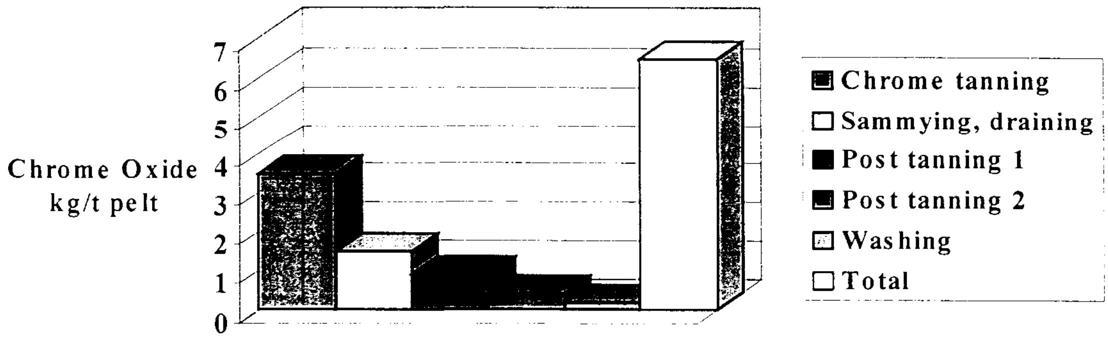
Tanning C - conventional, 1.9 % Cr_2O_3 on pelt weight
Tanning HE - high-exhaustion, 1.3 % Cr_2O_3 on pelt weight

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

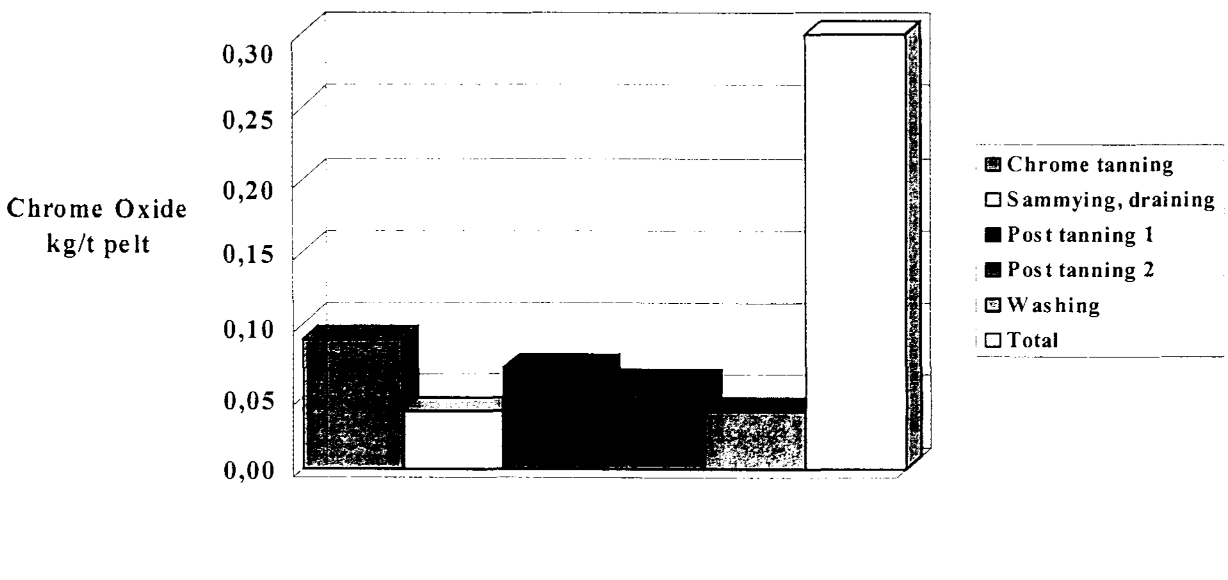
Figure 9
Unused chrome in residual floats from high-exhaustion and conventional tanning processes according to (13)

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



It follows from Figure 9 that chrome utilisation in a high-exhaustion tanning process increases up to 98 % while for conventional tanning a utilisation factor of 66 % is characteristic. The higher level of chrome utilisation leads to a significantly lower level of chrome concentration in residual floats. In a high-exhaustion tanning procedure, chrome leaching is minimal. 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 of 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.

The results of a high-exhaustion tanning process according to Example 2 above compared to a conventional chrome tanning can be seen in Table 3.

Table 3

Chrome concentration in residual floats from high-exhaustion and conventional tanning processes according to (12)

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
Neutralisation	0.02	0.01
Washing 2	0.01	0.01
Retanning, dyeing, fat liquoring	0.03	0.01
Washing 3	0.02	0.01

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

Implementing a procedure with increased collagen reactivity after adding glyoxylic acid to the pickle results in very high-exhaustion of the tanning float as well as excellent chrome fixing in the leather. The chrome offer may be reduced to some 1.0 - 2.0 % Cr_2O_3 depending on the pelt thickness without inducing any change in the chrome content of the leather (4.0 - 4.5 % Cr_2O_3) or its boil fastness.

Example 3: Final pH and temperature

The relationship between the final pH/temperature value and 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)

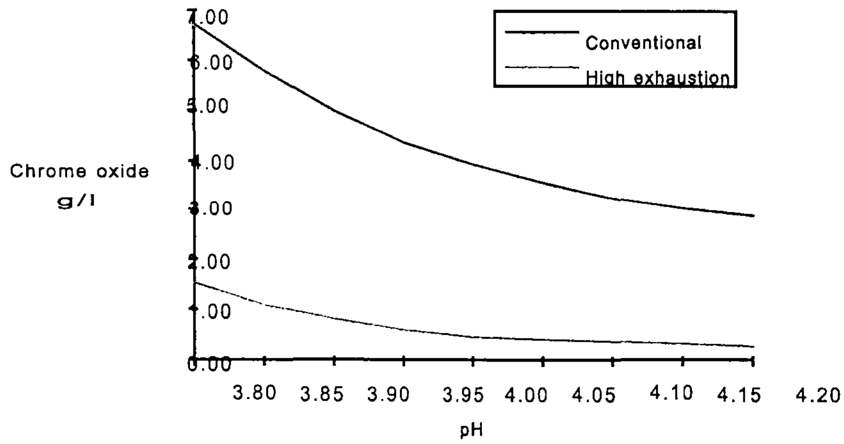
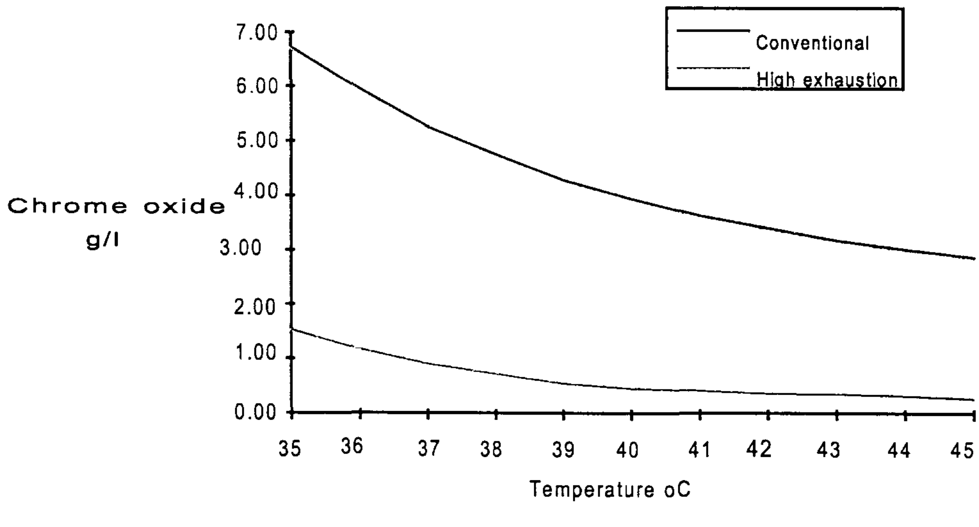


Figure 11
Effect of final temperature (oC) on chrome concentration in residual float from high-exhaustion tanning compared to conventional tanning according to (14)



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

Example 4: Chrome fixing in post-tanning

The chrome concentration in residual floats from post-tanning when using special polyacrylate dosed prior to neutralisation 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	-
Neutralisation/retanning	320	11
Washing 3	-	14
Fatliquoring/dyeing	218	11
Washing 4	83	7

Table 4 shows that after fixing the chrome with special polymer acrylate, chrome concentration in residual floats is around 10 mg/l, while it ranges between 200 - 500 mg/l when a conventional post-tanning procedure is applied. 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: Experience in Western Europe

Data based on practical experience tanneries In Western Europe have been collected and evaluated with respect to tanning efficiency (7, 16). Results of the evaluation are presented in Table 5 and graphically illustrated in Figure 12.

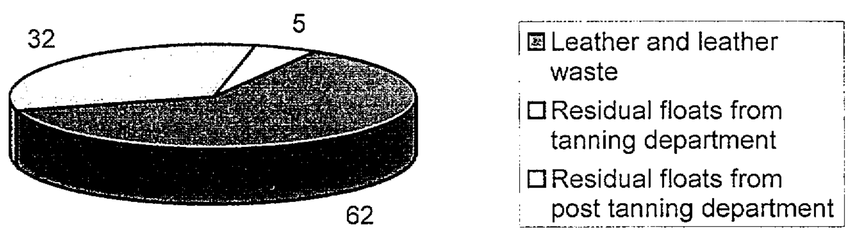
Table 5
Efficiency of high-exhaustion chrome tanning process compared to conventional process based on experience in Western Europe

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

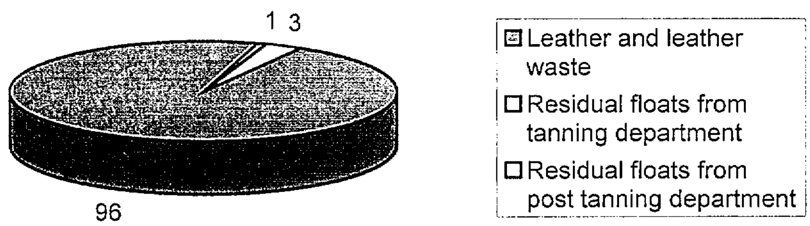
Tanning C - conventional
Tanning HE - high-exhaustion

Figure 12
Share of used/unused chrome in high-exhaustion process compared to conventional process, prcentage

Conventional tanning



High exhaustion tanning



The experience of tanneries in Western Europe confirms the attainability of very high chrome-exhaustion levels when using new tanning procedures. This very high degree of exhaustion results in a discharge of only 4 % of the chrome offer, while in conventional tanning the amount of chrome discharged is ten times greater. The chrome offer can be reduced by 35 % and chrome tanning materials can thus 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 in a modern tannery when assuming a water consumption of 30 m^3/t w/s hides at the most. Attaining this concentration makes it easier to handle the wastewater through direct/indirect effluent discharge and to meet local legislative limits on sludge landfills.

4. DIRECT CHROME RECYCLING

Recycling spent floats direct from chrome tanning back into processing is the simplest means of reusing chrome.

4.1. Recycling Techniques

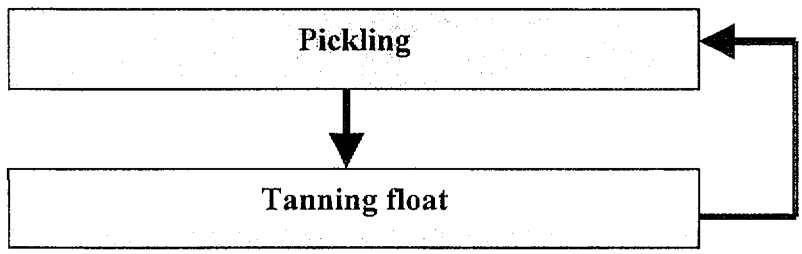
Several recycling techniques are employed industrially (16):

Option A

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

Figure 13

Recycling of spent tanning float to pickling

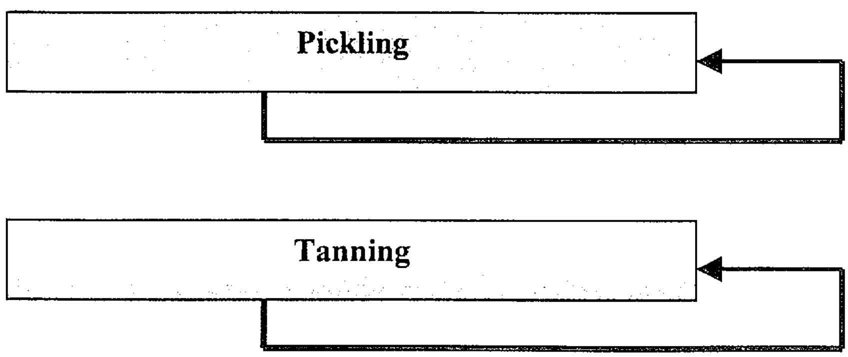


Option B

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

Figure 14

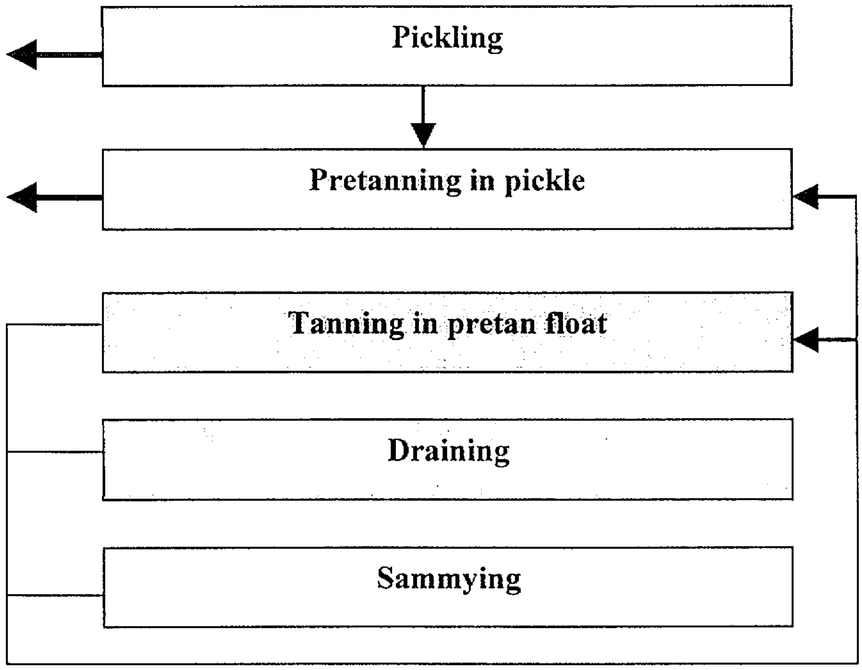
Separate recycling of spent pickling and tanning floats



Option C

A pre-tanning operation is inserted between pickling and tanning. Spent tanning floats mixed with draining and samm water are recycled in the following run pre-tanning and tanning. Certain quantities of the pickling and pre-tanning floats are discharged each day (Figure 15).

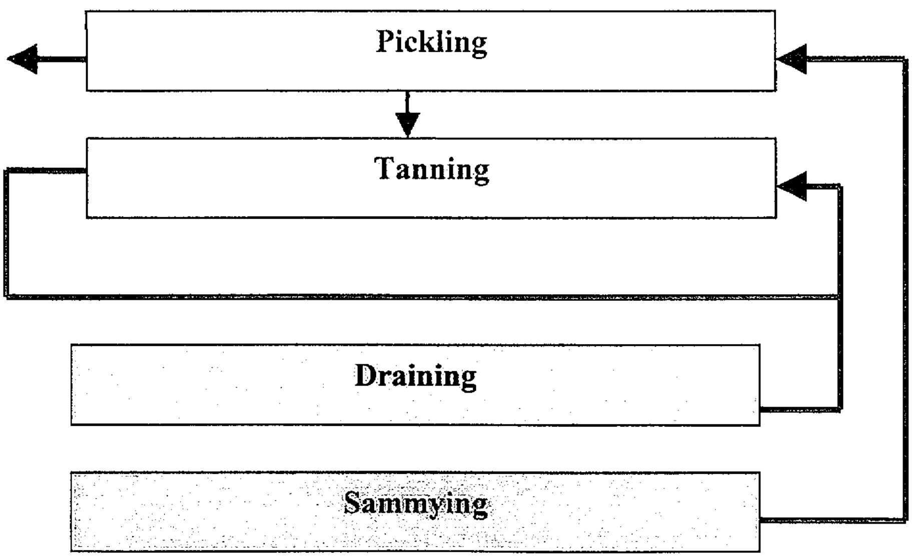
Figure 15
Recycling of tanning floats to pre-tanning and tanning



Option D

Spent tanning float mixed with draining water is recycled in the following tanning run. Samm water is recycled in the following pickling run and discharged each day(Figure 16).

Figure 16
Separate recycling of spent tanning floats and samm water



Other recycling techniques are also applied. Common to all techniques, however, is the need to remove leather fibre and other undissolved impurities by filtering the recycled floats. Thus, all recycling techniques used in tanning operations call for the installation of storage tanks, pumps and filters, all of which are commercially available.

Davies and Scroggie established a technological basis for chrome recycling (17). They demonstrated the importance of: (i) controlling and adapting the ionic strength of recycled floats so as to avoid acid swelling; and (ii) reaching equilibrium in the chemistry system after several cycles.

As a rule, neutral salts build-up occurs over five cycles ,whereafter they reach a steady state. Furthermore, it follows from experimental data that less reactive or inactive chrome complexes do not accumulate in the course of recycling tanning floats. Thus, the tanning process should not be negatively affected by recycling floats.

In direct chrome recycling, balancing the float volumes can cause some problems. The float volume required in the pickle is lower than the total volume of spent tanning float, plus draining/samm water. This is due to the fact that after deliming and bating, the spent float discharge is incomplete and the water content in pelt is higher (70 %) than that in wet blue (55 %). Adding pickle acids, dissolved chrome tannins and basifying agents also increases the volume of recycled spent floats.

Usually more float is available for recycling than can actually be used (6). This excess float must be discharged with effluent or treated in order to recover the chrome by precipitation. Alternatively, it might be used in re-tanning. Also in high-exhaustion tanning , the spent tanning float can also be recycled to make up the whole volume of the pickling float, thus preventing excess volume build-up.

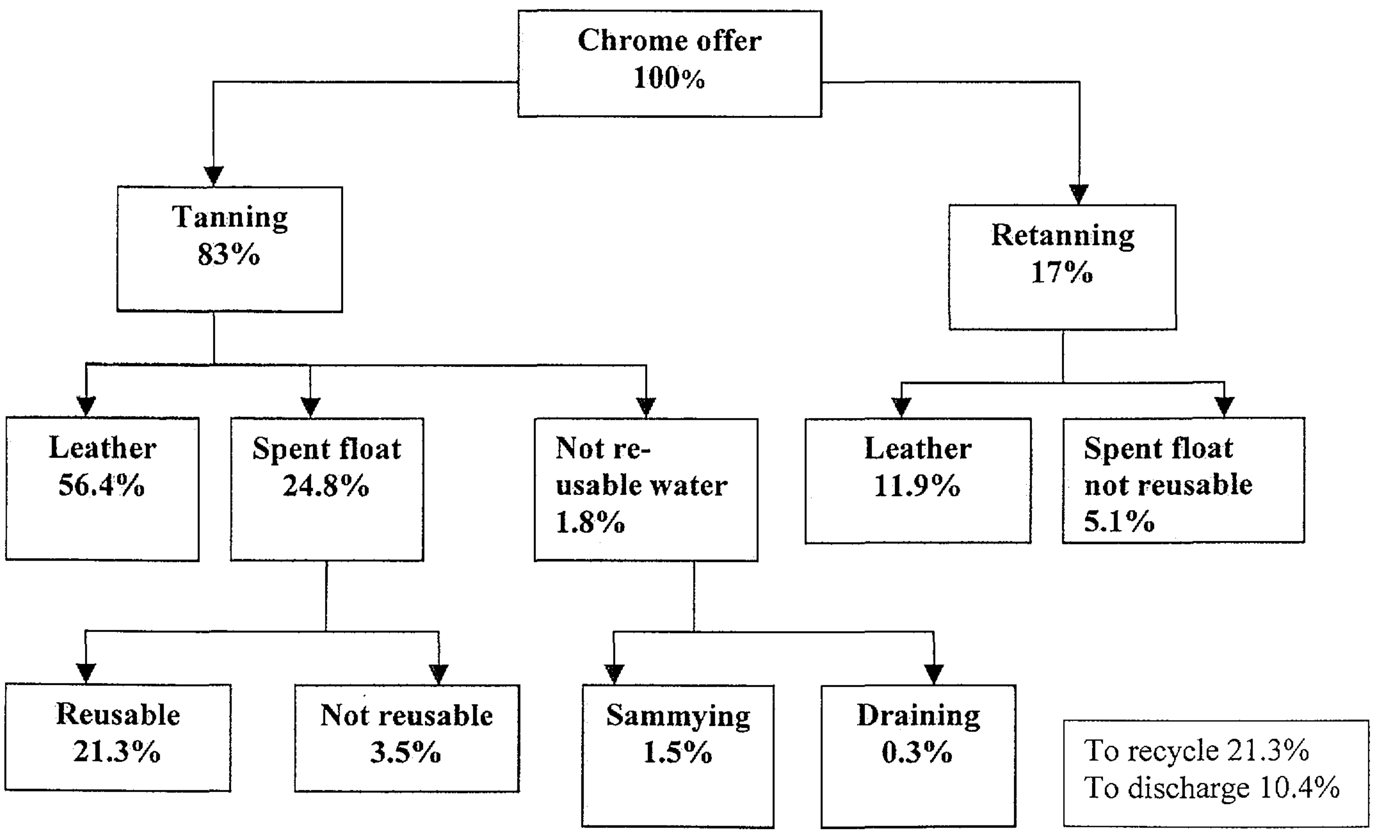
4.2. Recycling efficiency

A model for chrome distribution between leather and spent floats has been described with respect to reuse by direct recycling (6). Data related to chrome tanning/re-tanning 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/re-tanning efficiency 68 %



Other chrome distribution models can be constructed. The model in Table 6 and Figure 19 shows one such possibility. It follows from this model that 21 % of the chrome offer can be reused and saved by recycling the spent floats direct. Assuming a standard offer of 2.0 % Cr_2O_3 on pelt weight, i.e. 2.2 % Cr_2O_3 on w/s weight, and a water consumption of 50 m3/t hides, discharging 10 % of the chrome offer means that the concentration in mixed wastewater streams is 30 mg Cr/l. According to the model, a recycling technique can assure 90 % uptake of the chrome offer and the chrome load discharged in effluent is decreased to 1.5 kg Cr/t w/s hide.

Recycling efficiency depends primarily on the completeness of float collection, the rate of float excess to be dischargedand the recycling technique used. 90 % efficiency represents a standard that is easily attainable when recycling floats from conventional chrome tanning. Improved collection methods and more sophisticated recycling techniques makes the attainment of 95 - 98 % efficiency possible, whereupon the chrome load discharged in effluent drops to 0.30 - 0.75 kg Cr/t w/s hides. Under such circumstances, the chrome concentration in mixed wastewater streams may be assumed to be in the range of 10 - 25 mg Cr/l for water consumption at 30 m3/t hides.

5. CHROME RECOVERY

Recovering chrome from spent tanning floats after precipitation constitutes an indirect means of recycling and reusing the chrome in processing. By adopting indirect chrome reuse after precipitating the residual tanning floats, the tanner can avoid the problem of increasing float volume. In those cases where the chrome precipitated from floats contains numerous impurities, the chrome recovered is not reused; it is simply dumped.

5.1. Recovery and reuse

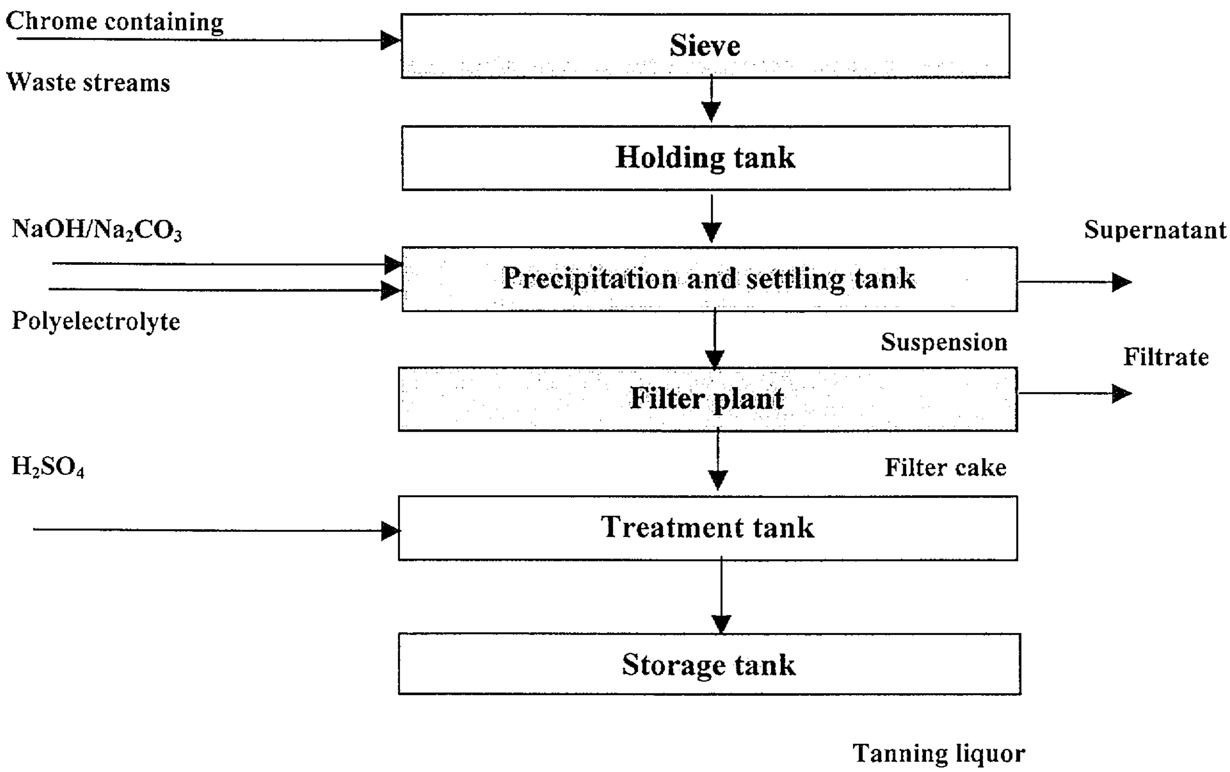
5.1.1. Recovery/reuse techniques

The principle is based on recovering the chrome from floats containing residual chrome by means of precipitation, separation and subsequent redissolution in acid for reuse. The base used to precipitate the chrome can vary. Two principal options offer themselves:

Option A

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

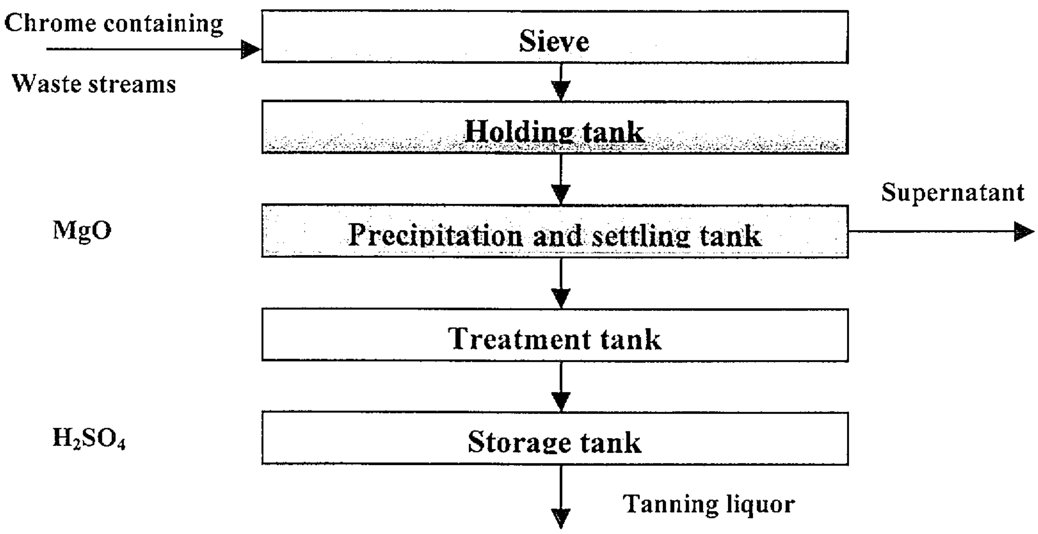
Figure 18
Flow Diagram of chrome recovery by precipitation with sodium hydroxide/carbonate



Option B

Slow precipitation with magnesium oxide, settling of the suspension, decantation of the supernatant (no need for a filter press) and subsequent acidification of 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; however, 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:

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

- Alkali (sodium hydroxide or carbonate) should be added slowly and stirred as a hot, nearly saturated solution: 110-120 % related to the stoichiometric ratio. Polymer flocculant is dosed as a solution prepared according to the producer's instructions. The amount should be checked experimentally.
- When using 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 properties.

- The optimum condition for precipitation is pH 8.5 - 9.0. Under standard conditions, the pH value should normally not exceed 10.0 because chromium hydroxide redissolves at a higher pH. When precipitating of floats from high-exhaustiontanning, it is sometimes useful to raise the pH over 10.0, reducing it thereafter to 8.5 - 9.0. When using MgO, the pH value should be in the range of 8.0 - 9.0; overdosage, however, is less likely.

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

- Precipitation usually takes up to 3 hours. When applying strong alkalis, a highly hydrated chrome oxide sludge drops down forming a suspension with very fine particles and long sedimentation/filtration time. Reduction of the high sludge volume is achieved by means of polymer flocculants.

- When precipitating with MgO, a hydrated chrome oxide sludge with a crystalline structure and short sedimentation/filtration time drops down. The solubility value of the chrome oxide hydrate produced is 2.9 x 10 - 29, i.e. extremely low, so that the precipitate is theoretically insoluble in water. In practice, however, the chrome concentration in the supernatant is about 5 mg/l

- The hydrated chrome oxide sludge has to be settled by letting it stand overnight or for 24 hours and then separating it from the supernatant by decanting.

- The thickened suspension of chrome oxide hydrate is dewatered by means of a filter technique, usually a filter press. The filter cake should have a dry substance content of at least 25 -30 %.

- The filter cake is dissolved by concentrated sulphuric acid being added at a rate of 2 kg or more per kg chrome oxide on a continuous basis, while stirring until pH 2.5 is reached. If necessary, additional heat should be supplied to raise the temperature of the mixture close to boiling point. 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 on standing. After adjusting its basicity, the tanning liquor is stored ready for re-use in a separate tank. , In those cases where in-house reduction is carried out, mixing chrome hydroxide precipitate with dichromate may be another way of achieving chrome reuse.

5.1.2. Recovery/reuse efficiency

In conventional chrome tanning, the chrome oxide content in the recovered liquor is usually 100 - 150 g Cr_2O_3/l. When recovering 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 chrome precipitation and redissolution. Nevertheless, if present in recovered chrome liquor, those compounds may sometimes cause problems in the production of high quality leather by imparting a greyish tint to the leather and impairing the consistency of shade.

It is recommended that attention be paid to the fat content in recovered tanning floats. A fat concentration of less than 45 mg/l in the recovered chrome liquor should be observed in order to prevent the leather discolouring. As for polymer flocculants, they do not interfere with the reuse of the chrome liquor produced, but contaminants are decomposed during the hot sulphuric acid solubilisation stage.

In general, if chrome recovery is performed incorrectly, certain problems can arise during tanning. For example, the problem of staining is a consequence of insufficient reduction of astringency in the reused spent float or inadequate solubilisation of the chrome precipitate.

Experience in India 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). When 50 % fresh chrome + 50 % recovered chrome were applied, some signs of an adverse effect on leather quality were to be observed. Using 75 % recovered chrome, distinct differences in quality were to be observed compared to the leather tanned only with fresh chrome. Given that only 25 - 30 % of the chrome offer is recoverable, adverse effects on leather quality need not be feared provided chrome recovery was properly carried out.

The tannery itself has to devise an optimal technology for applying the chrome liquor recovered. For example, if the tanning of grain leather is carried out using a powder tanning agent, the chrome liquor recovered can be used for split tanning. If the tanning is carried out using a fresh chrome liquor obtained by reducing the dichromates, the chrome liquor recovered can be used as a partial replacement: maximum 30 % of fresh chrome.

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

A model for chrome distribution between leather and spent floats has been described with respect to indirect chrome reuse by recovery (6). Corresponding data related to the chrome tanning/re-tanning efficiencies of 68 % and 90 % are presented in Table 7, as well as 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/re-tanning efficiency 68 %

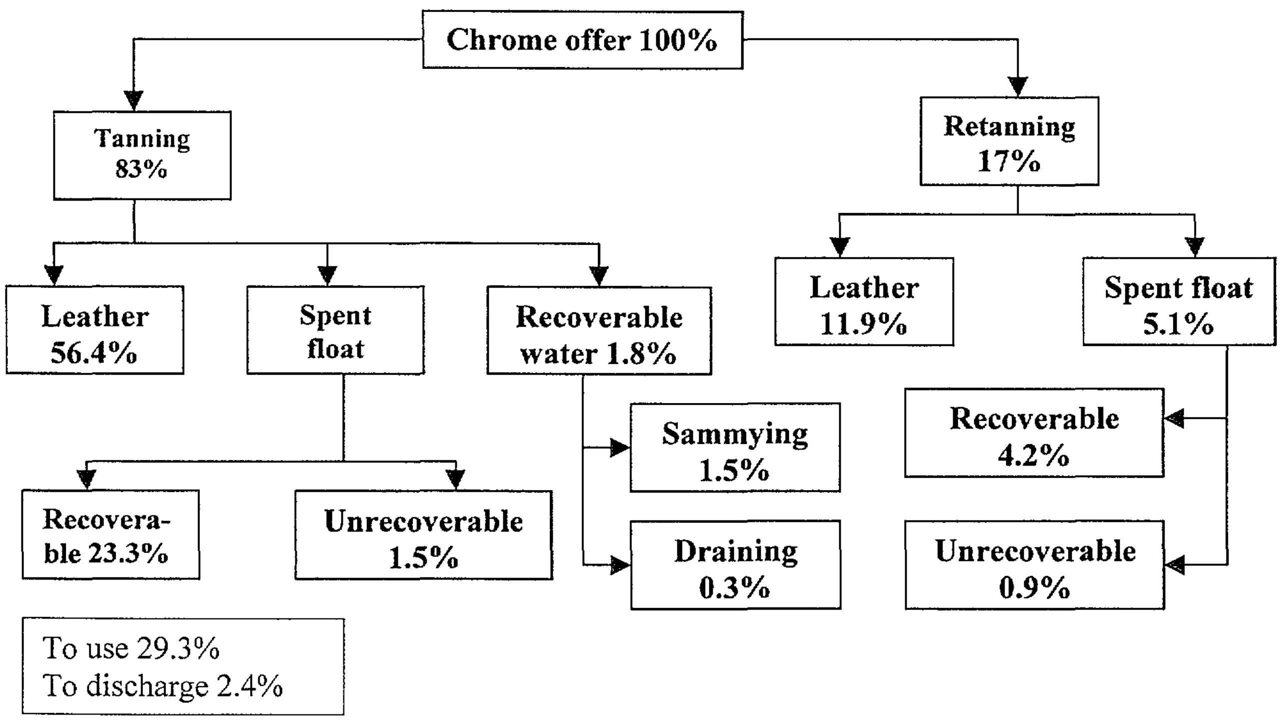
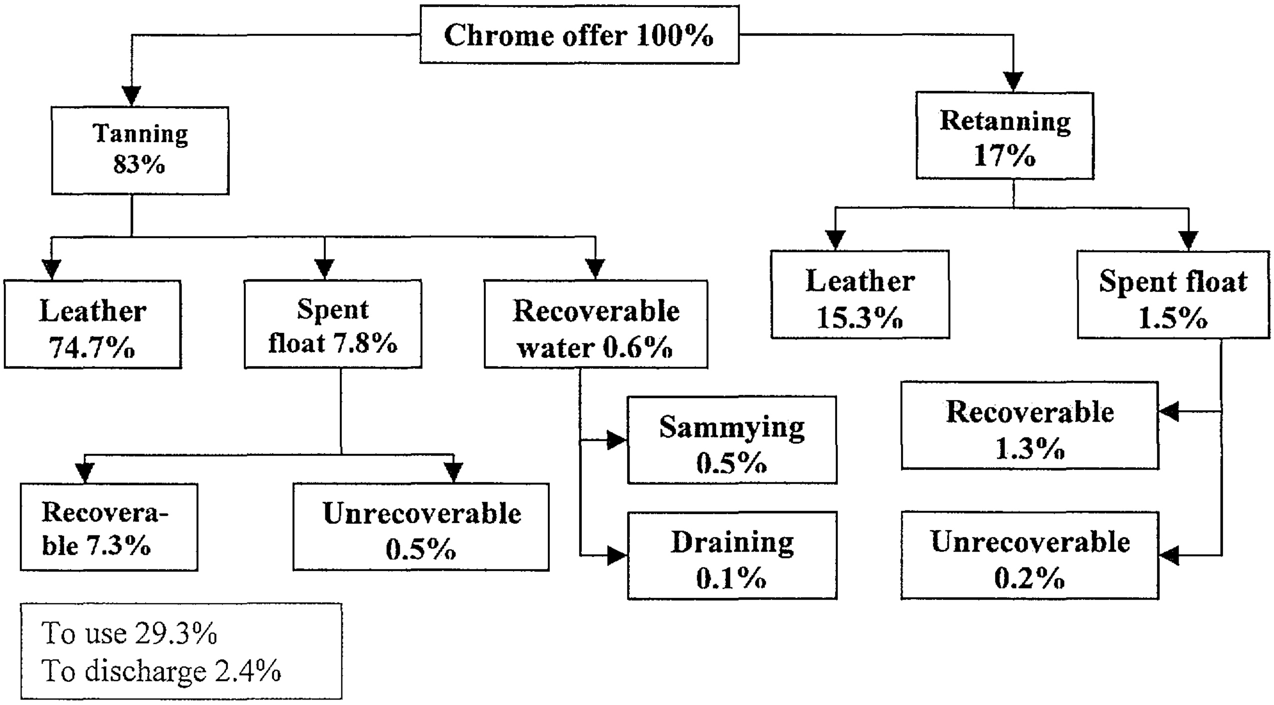


Figure 21
Chrome distribution scheme
Indirect reuse by recovery
Tanning/re-tanning efficiency 90 %



Whereas the model in Table 7, Figures 20 and 21 shows one such possibility, other chrome distribution models can be constructed.. It follows from this model that approximately 29 % of the chrome offer can be reused and saved by means of a recovery technique using precipitation when conventional tanning is applied and 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 %.

Assuming a standard offer of 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 in the amount of chrome discharged in effluent are shown in Table 8.

Table 8
Influence of chrome recovery/reuse upon tanning/re-tanning efficiency and amount of chrome 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 correctly performed chrome recovery/reuse reduces the chrome load discharged in effluents to 0.12 - 0.36 kg Cr/t w/s hides, whereupon the chrome concentration in the effluent ranges between 4 and 12 mg Cr/l. Residual amounts of unrecovered spent floats, leather fibres (viz. buffing dust), the supernatant and/or filtrate with a chrome content of 1 - 10 mg/l are sources of the residual chrome concentration in effluent. In order to reduce this concentration close to a value of 1 mg Cr/l, the residual floats from washing, neutralisation and fatliquoring must also be precipitated.

5.2. Recovery without reuse

In order to eliminate the chrome from residual floats to the greatest possible extent, all chrome- containing wastewater from post-tanning operations, together with tanning wastewater, have to be precipitated. Given the presence of organic substances in the residual floats emanating from neutralisation, re-tanning, fatliquoring and dyeing, the chrome precipitated cannot be reused.

Calcium hydroxide is the most frequently used precipitant. In order to achieve better full chrome precipitation, ferric and/or aluminium salt is added with the lime. In order to reduce the volume of precipitate, an organic polyelectrolyte should be added prior to settling and filtering.

A EU research project on the 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 l mg Cr/l in chrome containing waste streams. Selected results of large scale trials are summarised 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 - mixed wastewater 2	 321 460	 0.38 1.26
High fixation tanning - mixed wastewater	 27	 0.36

The results demonstrate that the chrome can be almost totally recovered by precipitation with lime and ferric chloride. A concentration of 1 mg Cr/l is attainable. Assuming a water consumption of 30 m3/t w/s hides, the residual chrome load discharged in effluent will be 0.03 kg Cr/t w/s hides. Sludge containing chrome cannot be reused; it must be deposited under in special landfill sites.

6. COST RATIOS

The actual extent of the chrome management implementation is governed by requirements pertaining to chrome concentration and/or chrome load discharged in effluent. The tanner has to apply whatever measures are necessary in order to meet local chrome regulations. The tanner is interested in corresponding technical and operational measures, as well as in chrome tanning procedures that are reasonably priced, yet do not affect the commercial value of the leather and its properties. The tanner's twin endeavours are to save chrome by increasing its utilisation factor and reduce in-process chrome losses.

Costs associated with improving chrome management should be related to the particular conditions of the given tannery. Notwithstanding, it is reasonable to provide a general example of the 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 performing a high-exhaustion tanning procedure in order to comply with regulations on the amount of chrome permissible in effluent will increase the operational chemical costs by 20 - 36 %. On the other hand, however, some 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 not only offers an important environmental benefit, but it also ensures cost savings in terms of fresh chrome and effluent treatment. The cost effectiveness depends on float collection efficiency, treatment efficiency, and capital and running costs.

Chrome recovery techniques have a direct bearing on capital and running costs. The choice between an alkali sodium salt and MgO is decisive in terms of capital costs since as a rule a filter press is not needed to dewater the chrome oxide precipitated with MgO. For a daily chrome recovery capacity of 12 - 15m^3 spent floats, capital costs of the following order can be expected:

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

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

As for running costs, details of the annual operating costs of an Indian chrome recovery plant are available (18). The corresponding data are summarised 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

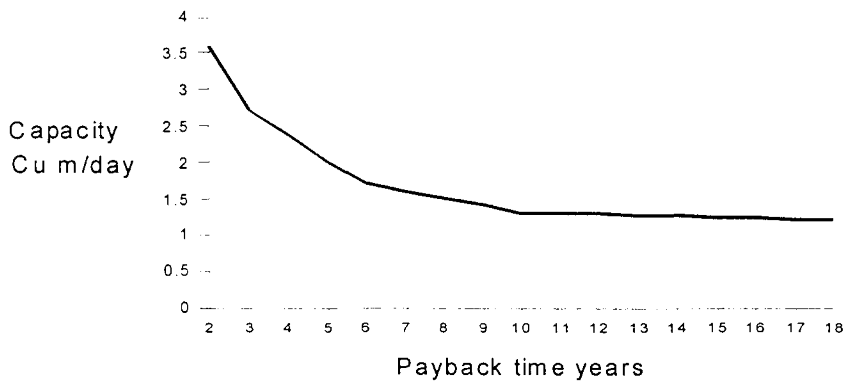
It can be seen from Table 11 that chemicals (MgO, sulphuric acid) represent a significant share (60%) of the operating costs. Prices for precipitants are dependent on where they are produced. Typical European prices are as follows:

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

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

Drawing on operational experience, the profitability of chrome recovery plant based on the use of MgO (14, 21) can be calculated. The profitability expressed in terms of the payback time is shown in Figure 22.

Figure 22
Payback Time as a Function of Recovery Plant Capacity



Assuming a reasonable payback period of three years, a chrome recovery plant based on the use of MgO would be profitable at a capacity as low as 2.5 m^3/day. Similar calculations with a longer payback period can also be made for a recovery plant using alkali sodium salt and mechanical dewatering. In general, the higher the recovery plant capacity, the greater the potential profitability.

Profitability levels are influenced by the total volume of spent floats recovered. In conventional chrome tanning, up to 30 % of the chrome offer contained in spent floats can be recovered. In addition, profitability may also be heightened by the 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 direct recycling technique, the following aspects deserve special mention:

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

From the economic standpoint, no general explicit recommendation can be made as to the optimum mode of reusing chrome from spent tanning/retanning floats.

7. ADVANTAGES AND LIMITATIONS OF VARIOUS METHODS

Securing a substantial increase in the utilisation of chrome in tanning operations is the touchstone of advanced chrome management. Chrome utilisation can be increased in three ways: high-exhaustion chrome tanning; direct recycling of spent floats; and chrome recovery/reuse. The efficiency of the various options has been described in the previous chapters. The circumstances essential to minimising the chrome load in effluent have also been evaluated. As a decision-making tool for tanners confronted with the task of choosing a suitable option, the features of the three options are summarised below in Figures 23-25.

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 minimised	**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	

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	

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, applicable to any type of leather	Higher running costs
No loss in leather quality	

8. CONCLUSIONS

The efficient and effective 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 traditional process less than 50 % of the chrome input is to be found in leather while more than 50 % is disposed in solid/liquid waste streams.

For this reason, chrome management aims at improving chrome utilisation in tanning processes to a maximum degree in order to minimise the amount of chrome discharged into effluent. Under normal conditions, only 60 - 80 % of the chrome offer is utilised 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 with a water consumption of 50 m^3/t w/s hides. This concentration is not acceptable according to current legislative limits in most countries.

In practice, three principal approaches to maximising chrome utilisation in tanning processes have been developed: high chrome uptake in tanning; direct tanning floats recycling; and chrome recovery/reuse after its precipitation and redissolving.

Optimising process parameters and **modifying the tanning process** 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 optimised.

Improved chrome uptake can be achieved by finishing the tanning at the highest possible pH and temperature levels. End-values up to 40 - 45°C and pH 4.0 - 4.2 are advantageous. Benefits are secured by using the lowest possible amount of chrome offer combined with a tanning time of maximum length and high drum speeds. Unless the tanning process is modified, a chrome offer lower than 1.7 % Cr_2O_3 on pelt weight is not recommended. It is reported that the amount of chrome discharged from a tanning operation fluctuates in a range of 2 - 5 kg Cr/t w/s hides. When optimising process parameters in order to increase the chrome uptake, the amount of chrome discharged in effluent is at the lower end of that range.

Modifications to the tanning process may involve masking the chrome tanning complexes and increasing collagen reactivity. A combination of process modifications and process parameter optimisation are the basis for modern high-exhaustion chrome tanning processes. Chrome utilisation in high-exhaustion tanning can be increased by up to 98 %. The chrome offer can be reduced from a standard level 2.0 % Cr_2O_3 to 1.3 % Cr_2O_3 on pelt weight depending on the pelt thickness, yet without affecting the leather quality. Chrome leaching in post-tanning operations can also be minimised; it requires an improved drum drive system and an increased level of process control. High-exhaustion tanning can result in a discharge of only 0.4 kg Cr/t w/s hides. In a modern tannery, a concentration of 13 mg Cr/l may be expected in mixed waste water streams when assuming maximum water consumption of 30 m^3/t w/s hides.

The direct recycling of spent floats from chrome tanning back into processing is the simplest form of reusing chrome. The industry employs several recycling techniques. Using

a simple recycling technique, 90 % efficiency can be attained. Efficiency, however, is limited by a build-up of excess liquor volume. Better float collection and more sophisticated

recycling technique contribute to the attainment of 95 - 98 % efficiency, where after the amount of chrome discharged in effluent drops to 0.30-0.75 kg Cr/t w/s hides. This, too, calls for an increased level of process control and some capital investment.

Chrome recovery is an indirect way of recycling chrome in leather production. It enables the tanner to avoid problems attributable to the accumulation of float volume. In principle, it entails recovering the chrome from floats containing residual chrome by means of precipitation and separation of suspension, before ultimately redissolving it in acid for reuse. Variations arise in terms of the alkali used to precipitate the chrome (sodium hydroxide/carbonate, magnesium oxide) and the need to apply a filtration technique. Higher capital and running costs are to be expected.

The choice between high-exhaustion tanning, direct float recycling and indirect recovery/reuse depends on individual conditions in the tannery concerned. No explicit recommendation can be made as to the optimum way of reusing the chrome and reducing it to a minimal level in the wastewater stream.

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

The lowest practically attainable amount of chrome in effluent lies somewhere between 0.3 and 0.4 kg Cr/t w/s hides. Thus, with a standard effluent production of 30 m^3/t w/s hides, the chrome concentration ranges between 10 and 14 mg Cr/l. However, legislative requirements most frequently stipulate a range of 1-4 mg Cr/l, thus making it mandatory to precipitate all waste streams from tanning/post-tanning operations, once the chrome has been recovered. Calcium hydroxide combined with ferric and/or aluminium salt is considered the most suitable precipitant. Only after precipitation, can a concentration of about 1 mg Cr/l (corresponding to an amount of 0.03 kg Cr/t w/s hides) be attained.

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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

Abstract

Securing a substantial increase in the utilisation of chrome in tanning operations is the touchstone of advanced chrome management. Chrome utilisation can be increased in three ways: high-exhaustion chrome tanning; direct recycling of spent floats; and chrome recovery/reuse. Focused on maximising chrome utilisation and recovery in tanning processes and minimising the amount of chrome discharged, the paper is designed to assist tanners in choosing the option best suited to their specific operational requirements. The paper describes the efficiency of the various options and evaluates the circumstances essential to minimising the chrome load in effluent. It also provides extensive material on chrome tanning, recovery and recycling techniques and the cost ratios, supplemented by a series of summary tables.