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

MASS BALANCE IN LEATHER PROCESSING

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INTRODUCTION

The essential part of any tannery waste audit is assessing the efficiency of existing operations carried out during the leather manufacturing process. Typically, tannery staff have a good idea of, and comparatively accurate figures on, the waste resulting from specific operations such as fleshing, splitting, trimming or chrome tanning. Only rarely, however, do they have a proper overview of the entire range of waste generated. Thus, when considering various cleaner technologies or waste treatment systems, having access to a complete computation of the overall mass balance certainly makes it easier for a tanner facing arduous choices. Dialogue with environmental authorities is also simpler if such figures are readily available.

This paper attempts to provide a comprehensive computation of a mass balance and the efficiency of the leather manufacturing process for a tannery, seen as a closed entity. The calculations are deliberately based on operations in a hypothetical tannery processing bovine hides and producing upper leather for shoes. With minor exceptions (batch washing instead of continuous rinsing, splitting in lime, roller coating), it follows the conventional process. The figures, however, are derived from various, specific shop-floor data, personal experience and estimates, as well as from literature. The process formulae are given in Annex 1.

Inevitably, given the well-known, wide variations in raw materials, processing methods and equipment used, and the variances in final product specifications, certain basic assumptions had to be made. These are summarised in the introductory table overleaf. For the sake of simplification, some aspects of the process have been disregarded (energy balance) or not fully elaborated (water balance in drying). To our mind, that does not significantly affect the overall picture.

Following the traditional pattern, the entire process has been subdivided into four main processing stages: beamhouse, tanning, post-tanning and finishing. For each stage, a flow-diagram shows the main operational steps. Separate (sub)calculations have been made for grain and usable splits. Although not strictly part of the tannery process, the balance of raw hides preservation using wet salting, which has a major effect on tannery pollution balance, has also been included in the study (see Annex 2).

The model used in this paper shows that only 53% of corium collagen and 15% of the chemicals purchased are retained in the finished leather. The challenge over the next decade will be to reduce this profligate waste of resources.

While we found that our mass balance computation corresponds reasonably well with the situation in some factories, there is no doubt that figures in many others may differ considerably. Nevertheless, we trust that tanners will find this paper a useful reference source and a suitable tool when making their own calculations.

MASS BALANCE OF LEATHER PROCESSING

PREMISES - ASSUMPTIONS

Raw hide	**1000 kg of wet salted cattle hides** *(39 pieces, green weight 1100 kg)* Weight class: 25 - 29.5 kg green weight, *about 25.6 kg salted weight per hide* Area per hide: *Average 4 m^2/hide* Total area: 156 m^2 Thickness: about 6 - 8 mm Density: 0.9 - 1.2 g/cm^3
Conventional technology *For full recipe please refer to Annex 1 !*	Liming: Hair-burning Fleshing: After liming Deliming: Ammonium salt/acid Tanning: Conventional chrome tanning with 2 % Cr_2O_3, chrome extract 25 % Cr_2O_3, 33 % basicity, neither high exhaustion nor chrome recovery/ recycling applied Splitting: In the blue state *Mass balance for beamhouse (only) also calculated for splitting after liming* Retanning: Grain with chrome and organic tanning, split without chrome retanning *The amount of active substance in organic tanning, fatliquors and dyes used in wet finishing assumed to be about 75 %, the degree of exhaustion approximately 80 - 90 %.* Finishing: Partially solvent-free, applied by a combination of curtain-and roller-coating and spraying.
Leather	**Shoe upper:** Lightly corrected grain Thickness: about 1.8 mm Apparent density: about 0.8 g/cm^3 **Chrome split:** Conventional embossing finish Thickness: about 1.2 mm Apparent density: about 0.8 g/cm^3
Weight ratios and yields	Wet salted weight: 1000 kg Limed (pelt) weight: 1100 kg Shaved weight, grain: 262 kg Shaved weight, split: 88 kg Finished leather, grain: 195 kg - 138 m^2 Finished leather, split: 60 kg - 60 m^2 Finished leather, grain: 12.5 dm^2/kg reenweight Finished leather, split: 5.4 dm^2/kg green weight Finished leather, total: 17.9 dm^2/kg green weight

Beamhouse work

The raw material processed in the beamhouse is wet salted hides obtained by curing, an operation which is normally carried out elsewhere (see Annex 2). For better clarity three main components have been defined:

- **Corium:** collagen containing the true "leather-building substance"
- **Epidermis:** mainly hair, cells and certain protein-like substances that are removed through liming
- **Subcutis (subcutaneous tissue):** collagen and certain other proteins including fats, that are removed by fleshing during beamhouse processes (**flesh**).

For the same reason, substances of lesser quantitative importance such as soluble proteins and proteo-glycanes have been disregarded. The typical composition of a wet salted hide is given in Figure 1 below.

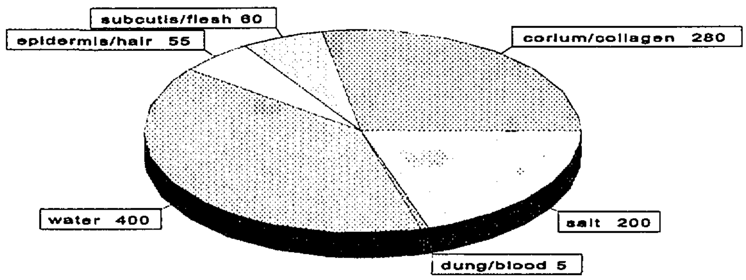


Figure 1. Main components of wet salted raw hides
In kg/1000 kg of wet salted hides

In order to ensure the correct calculation of the mass balance in the beamhouse, it is very important to establish whether splitting takes place after liming or after chrome tanning. Whereas most tanners today prefer splitting ex-lime primarily for environmental reasons (as it reduces the amount of chrome containing solid waste and - as some claim - ensures better quality and/or greater yields), many tanners still practice ex-chrome splitting ("in the blue").

For this reason both possibilities have been taken into consideration when illustrating the process flow in the beamhouse (see Figure 2).

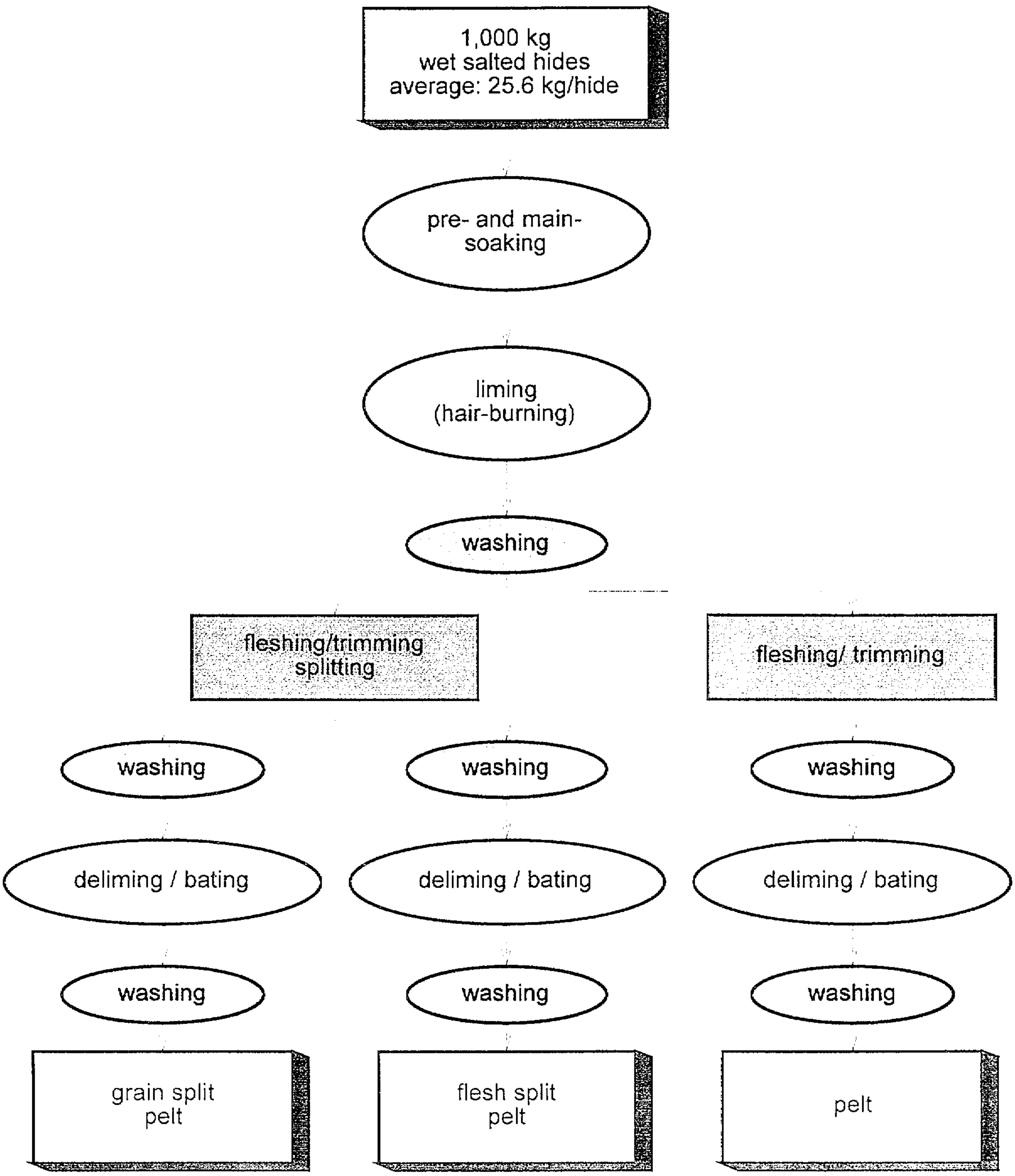


Figure 2. Flow diagram of beamhouse operations
Left: splitting after liming *Right: without splitting*

During the beamhouse processes, certain raw hide components are separated in various forms. As a rule, the chemicals added do not remain in the hides: acids and ammonium salts react with $Ca(OH)_2$ and the Na_2S is oxidized. Certain - almost negligible - amounts of NH_3 and H_2S escape into the air. This, however, which is disregarded when computing mass balance in the beamhouse.

Trimming and fleshing take place after liming, although in practice some tanners trim and flesh in green. This applies regardless whether the hides are split in lime or blue.

Depending on such factors as raw hide characteristics, technology and range of final products, the amount/weight of unsplit pelts, splits (grain and flesh), trimmings and fleshings varies widely. The data given in Figure 3 are to be seen as typical average values.

WITHOUT SPLITTING				SPLITTING AFTER LIMING		
COMPONENT	INPUT	OUTPUT		COMPONENT	INPUT	OUTPUT
	kg	kg			kg	kg
Wet salted raw hide	1000	0		Wet salted raw hide	1000	0
Process water	17000	0		Process water	16700	0
Effluent	0	16300		Effluent	0	16000
Tenside	3	3		Tenside	3	3
NaCl	0	200		NaCl	0	200
$Ca(OH)_2$	40	40		$Ca(OH)_2$	40	40
Na_2S	25	25		Na_2S	25	25
Ammonium salts	27	27		Ammonium salts	17	17
Acids	9	9		Acids	0	0
Enzyme	5	5		Enzyme	3	3
Fleshings	0	300		Fleshings	0	300
Trimmings	0	100		Trimmings	0	100
Unusable split	0	0		Unusable split	0	155
Unsplit pelt	0	1100		Unsplit pelt	0	0
Grain split	0	0		Grain split	0	750
Flesh split	0	0		Flesh split	0	195
TOTAL	**18 109**	**18 109**		**TOTAL**	**17 788**	**17 788**

Figure 3. Mass balance: beamhouse without splitting and splitting after liming

The composition of fleshings and trimmings also varies widely. The mass balance in Figure 4 is based on average values.

Component	Fleshings		Trimmings	
	kg	%	kg	%
Water	240	80	70	70
Collagen	24	8	18	18
Salts	24	8	9	9
Fats	12	4	3	3
TOTAL	**300**	**100**	**100**	**100**

Figure 4. Composition of fleshings and trimmings

2. Chrome tanning

To all intents and purposes, the pelt, i.e. the raw material entering the tanyard, is virtually only composed of collagen and water; the small amount of fat, salts (e.g. calcium salts) and tensides that remain after beamhouse operations have been disregarded in the computation. The typical composition of a pelt prior to tanning is shown in Figure 5.

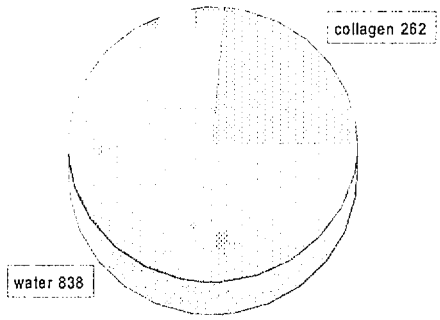


Figure 5. Main components of pelt *(kg/1100 kg pelt weight)*

The main steps in a tanyard using conventional technology, i.e. not using any type of recycling, high exhaustion or chrome recovery process, are shown in Figure 6.

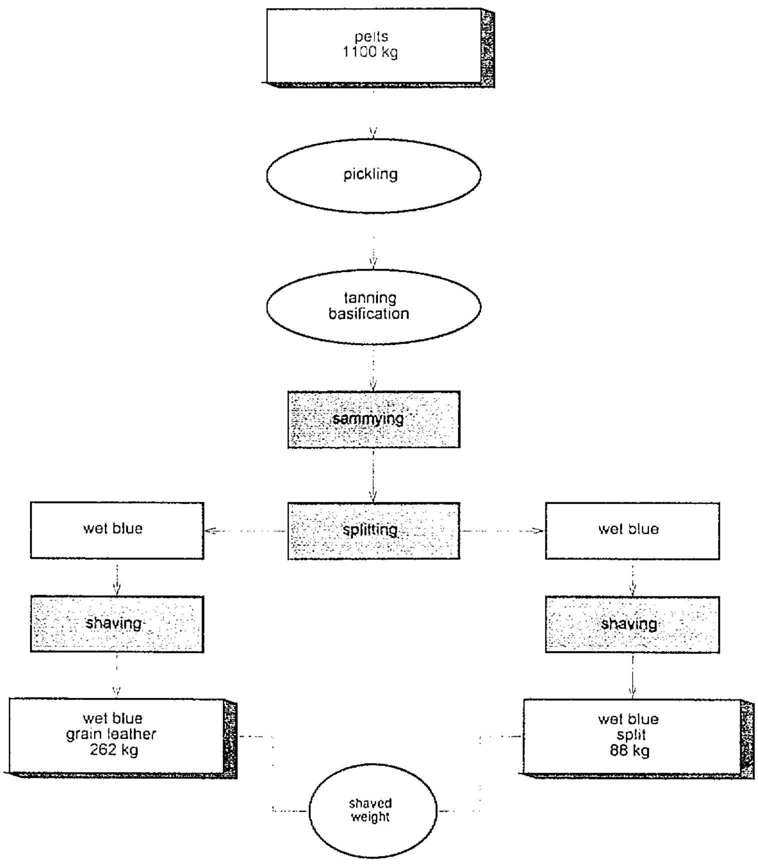


Figure 6.Flow diagram of chrome tanning of unsplit pelt

As mentioned earlier, the mass balance has been calculated for tanning unsplit pelt; total mass balance, however, is not significantly affected, should the grain split and flesh split be tanned separately.

The products resulting from tanyard operations are grain leather, usable splits and a certain amount of unusable splits, i.e. chrome-containing solid waste. The desired thickness of the grain leather defines the weight ratio of the grain-to-flesh split which, in turn, depends on the specification of the final product.

At the end of chrome tanning, some 75 per cent of the chrome offer (Cr_2O_3) remains in the collagen structure. Small amounts of other chemicals and auxiliaries such as tensides, acids and bases (in the form of soluble 'reaction salts') remain in the wet blue leather. The presence of calcium is very common and occasionally causes irregular dyeing. In terms of weight, all such residues can be disregarded.

Calculation of the chrome balance:

Offer: Chrome extract containing 25% Cr_2O_3 and about 40% Na_2SO_4 in the amount of 8%, corresponding to 2% Cr_2O_3 on pelt weight

Exhaustion: About 75%: about 1.5% Cr_2O_3 reacts with the collagen of the pelt in the form of a bi-nuclear basic chrome sulfate complex.

Cr_2O_3 : $Cr_2(SO_4)(OH)_2$ ratio: 152 : 234 (f: Cr_2O_3 x 1.55)

COMPONENT	INPUT	OUTPUT
	kg	kg
Pelts	1100	0
Process water	1300	0
Effluent	0	1650
NaCl	55	55
H_2SO_4/HCOOH	11	0
Chrome extract (25% Cr_2O_3)	88	62
MgO/$NaHCO_3$	8	0
Reaction salts		19
Grain leather (wet blue)	0	262
Split leather (wet blue)	0	88
Unusable split	0	107
Trimmings	0	20
Shavings	0	99
Sammying water	0	200
		0
TOTAL	**2 562**	**2 562**

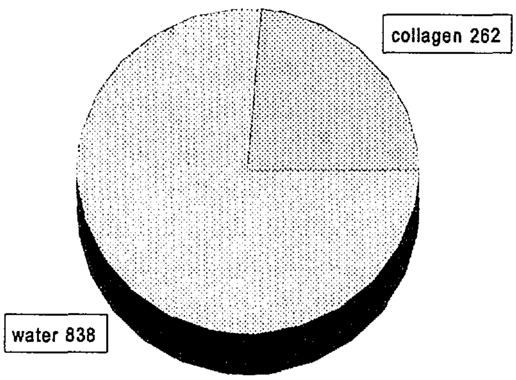
Figure 7. Mass balance of the tanning process

The primary concern of tanners and environmental protection authorities alike is the chrome balance. The issues at stake are: how much chrome remains in the grain leather and splits? And how much is discharged in solid waste and effluent? A typical distribution for a conventional main tanning process is shown in Figure 8.

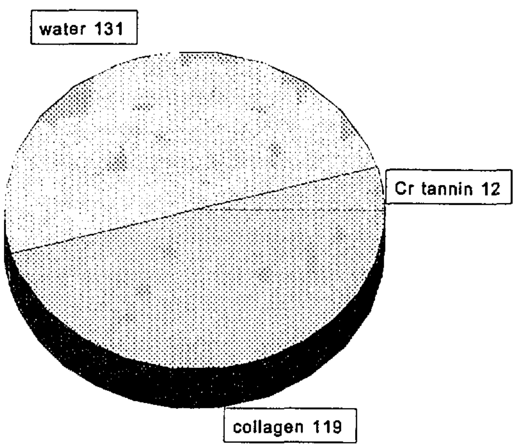
Chrome offer calculated as:	Chrome input %	kg	In grain leather kg	In usable split kg	In solid waste kg	In effluent kg
Basic chrome sulfate (extract)	8	88	-	-	-	62
Bi-nuclear complex	-	-	12	4	10	-
Cr_2O_3	2	22	7.5 (34%)	2.5 (11%)	6.5 (30%)	5.5 (25%)

Figure 8. Chrome balance of the main tanning process
Input: % and kg/1 100 kg limed pelt weight; Output: kg

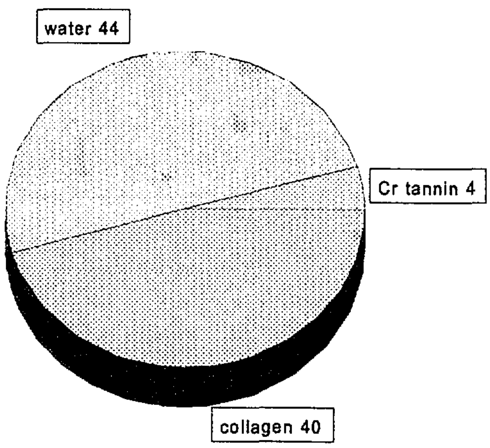
The composition of the resulting wet blue reflects the change the pelt has undergone during the chrome tanning process (Figure 9).



Pelt: 1100 kg



Wet blue grain leather: 262 kg



Wet blue split leather: 88 kg

Figure 9. Composition of pelt, wet blue grain leather and wet blue split leather
Chrome tannin calculated as bi-nuclear chrome sulphate complex

3. Post-tanning (wet work)

At this stage of manufacture, the starting material is wet-blue grain leather and splits, the composition of which was shown in Figure 9. The variety of and differences in post-tanning wet work formulations followed by tanners (even when producing very similar types of leather) is much broader than in beamhouse and chrome tanning. Nevertheless, whereas the chemicals used, float length, duration, temperature and sequence may differ, several steps involved in converting wet blue (both grain leather and splits) into crust leather can be considered typical for most tanneries.

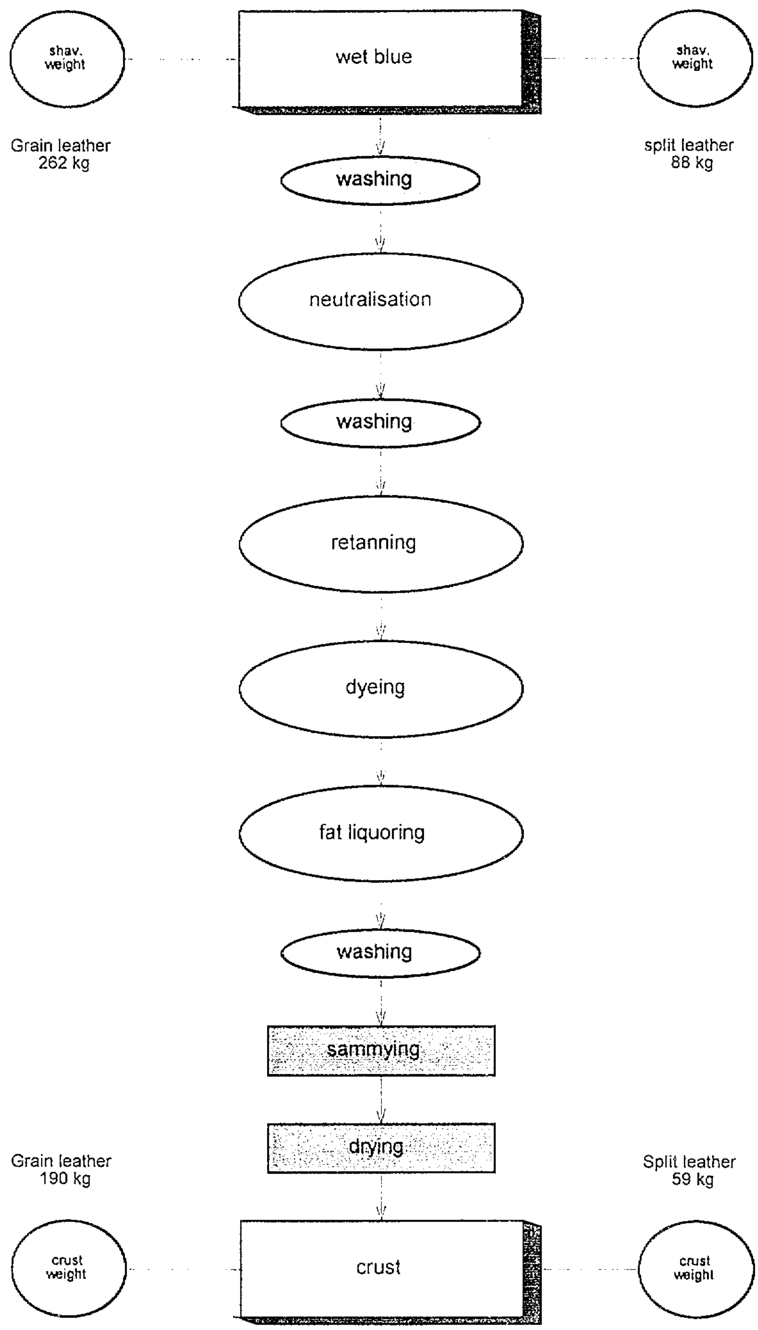


Figure 10. Flow diagram for post-tanning wet work of wet-blue grain leather and split

The amount of chemicals, i.e. the additional components absorbed and retained by leather in wet finishing, depends primarily on the offer (quantity) of a certain chemical, its active substance content and degree of exhaustion (Annex 1). A typical mass balance for wet-finishing operations is given in Figure 11 (grain leather) and Figure 12 (split).

COMPONENT	INPUT	OUTPUT
	kg	kg
Grain leather wet blue (50% H_2O)	262	0
Process water	4400	0
Effluent	0	4400
Vacuum drying water*	0	104
$NaHCO_3$/HCOONa	8	8
Chrome extract (25% Cr_2O_3)	13	9
Organic tannins	20	4
Fatliquors	15	3
Dyestuffs	4	1
Acids	4	4
Leather waste (fibers)	0	3
Grain leather crust (14% H_2O)	0	190
		0
TOTAL	**4 726**	**4726**

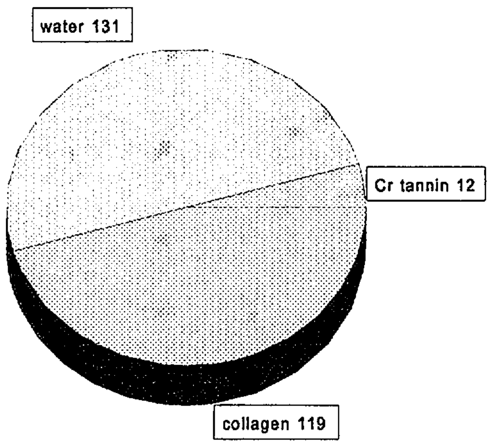
Figure 11. Mass balance of post tanning operations - wet blue grain leather

COMPONENT	INPUT	OUTPUT
	kg	kg
Split leather wet blue (50% H_2O)	88	0
Process water	1500	0
Effluent	0	1500
Vacuum drying water*	0	35.8
$NaHCO_3$/HCOONa	2.6	2.6
Organic tannins	5.3	1.0
Fatliquors	6.2	1.2
Dyestuffs	1.3	0.2
Acids	1.3	1.2
Leather waste (fibers, trimmings)	0	4
Split leather crust (14% H_2O)	0	59
TOTAL	**1 605**	**1 605**

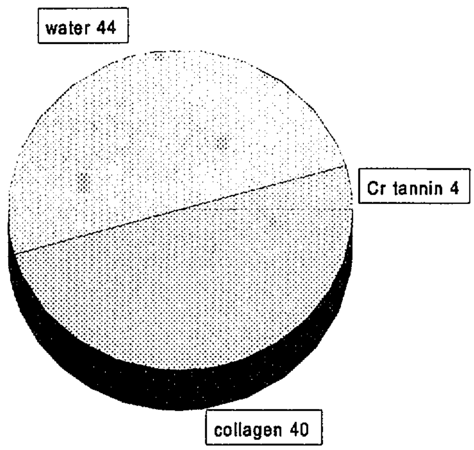
Figure 12. Mass balance of post tanning operations - wet blue split leather

**Only water evaporation taken into account*

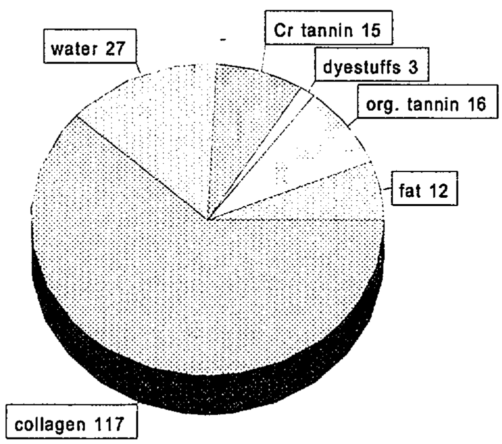
The composition of crust leather reflects the change in wet blue due to post-tanning processes (Figure 13).



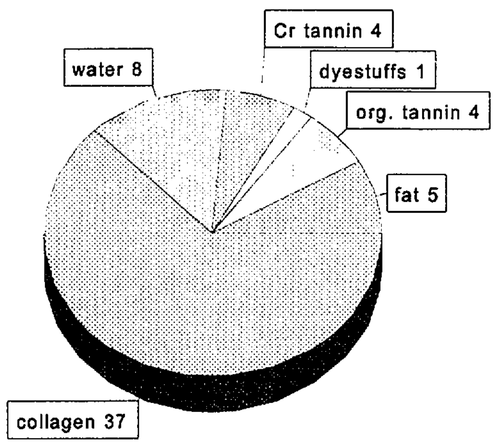
Wet blue grain leather: 262 kg



Wet blue split leather: 88 kg



Crust grain leather: 190 kg



Crust split leather: 59 kg

Figure 13. Composition of wet blue and crust grain leather *(left)* and wet blue and crust split leather *(right)*.

4. Finishing

It is hardly possible to find two tanneries following exactly the same finishing procedure and, more particularly, the same finishing formulation even when they use the same raw material in order to produce the same type of finished leather. Furthermore, the operational differences in finishing grain leather and splits are considerable. Typical operations in a finishing department are shown in Figure 14.

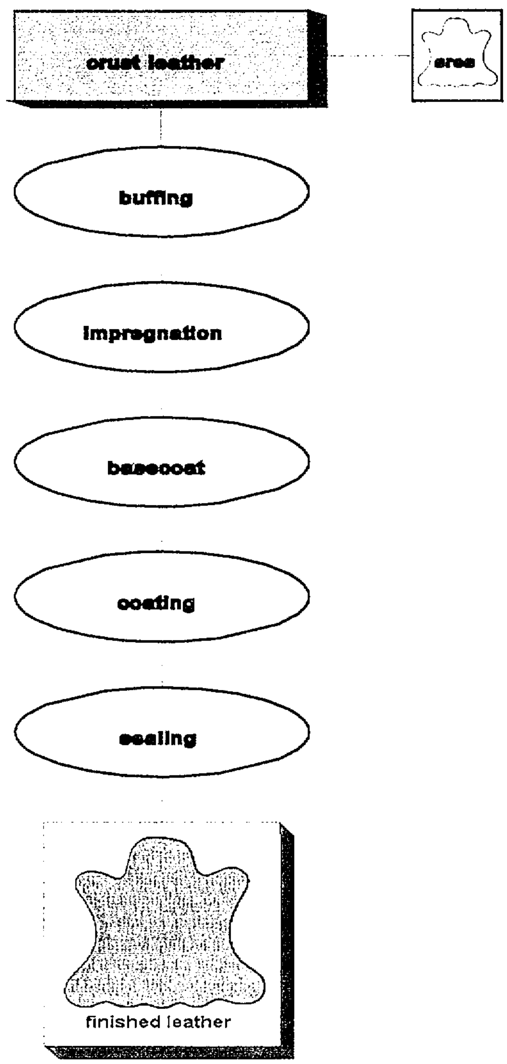
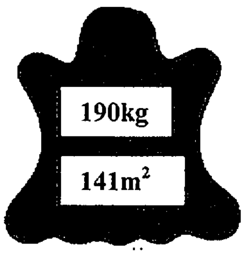


Figure 14. Flow diagram of finishing of crust leathers (grain and split)

Although as a rule crust leather is not measured, it is possible to determine its area using a weight/area ratio that can be established on the basis of thickness and apparent density (see introductory table on basic assumptions).

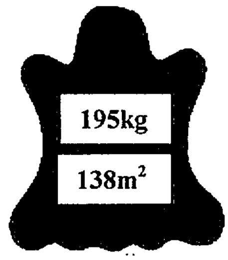
The amount of chemicals needed for coating is always calculated according to area: in grams per square metre (g/m^2). Finishing chemicals are normally supplied and subsequently applied in liquid form. The active ingredient component is expressed in terms of dry matter content . The amount required and ultimately applied is determined on that basis.

Loss of chemicals, trimmings and water consumption were taken into account when calculating the mass balance in finishing (Figures 15 and 16).



Grainleather leather

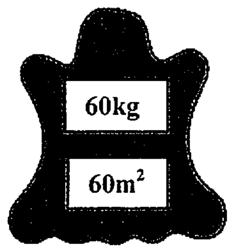
Chemicals: binder(s), pigments, solvents, water, auxiliaries	
INPUT	
Dry substances	11 kg
Solvents	28 kg
Water	35 kg
Wet finish (total)	74 kg
OUTPUT	
Dry substances	1 kg
Solvents	28 kg
Water	35 kg
Loss by overspray etc. (Total)	64 kg
Actual dry substance added	10 kg
Buffing dust:	1 kg
Off-cuts:	4 kg
Net weight increase:	5 kg



Finished grain

Figure 15. Mass balance: Finishing of grain leather (*in kg/141 m^2 crust grain leather*)

Chemicals: binder(s), pigments, solvents, water, others	
INPUT	
Dry substances	3 kg
Solvents	12 kg
Water:	11 kg
Wet finish (total)	26 kg
OUTPUT	
Dry substances	1 kg
Solvents	12 kg
Water	11 kg
Loss by overspray etc.. (Total)	24 kg
Actual dry substance added	2 kg
Buffing dust:	-
Off cuts:	1 kg
Net weight increase	1 kg



Finished embossed split

Split leather

Figure 16. Mass balance: Finishing of split leather (*in kg/61 m^2 crust split leather*)

5. Efficiency of leather manufacturing

5.1. Collagen

When evaluating the efficiency of leather manufacture, one of the main criteria is the actual utilisation of collagen. To obtain a true picture of collagen balance, a distinction was made between the **corium collagen** (true leather-building substance) and **total collagen** (corium and subcutis/flesh collagen). The 'fate' of both categories throughout the process is shown in Figure 17 (Compare also Figures 2, 5, 9 and 13). As mentioned in the introductory table of basic assumptions, the starting material is 1,000 kg wet salted hides.

Component	Amount of collagen		
	kg	% of corium collagen	% of total collagen
INPUT			
Corium collagen (Leather building collagen)	280	100	92
Subcutis collagen	24	-	8
Total collagen input	304	-	100
OUTPUT			
Grain leather	113	40.0	37.2
Split leather	36	13.0	11.8
TOTAL COLLAGEN IN FINISHED LEATHER	**149**	**53.0**	**49.0**
Fleshings	24	from subcutis	8.0
Trimmings	18	6.5	6.0
Unusable chrome split	49	17.5	16.1
Shavings	45	16.0	15.0
Wet blue trimmings	9	3.0	2.8
Crust leather waste	5	1.8	1.6
Buffing dust	1	0.4	0.3
Finished leather off-cuts	4	1.6	1.3
TOTAL COLLAGEN IN SOLID WASTE	**155**	**47.0**	**51.0**
Total collagen output	**304**	**100**	**100**

Figure 17. Collagen distribution wet salted hide, finished leather and solid waste
(Starting material: 1,000 kg wet salted raw hides, splitting in chrome)

Evidently, only 53 per cent of the corium collagen and about 50 per cent of the total collagen content of the raw hide end up in the finished leather. The rest is very often disposed of as part of solid waste, since for various reasons (lack of markets, commercial viability, inadequate technology etc.) recovery of valuable components such as collagen, fat or chrome is not practised (Figure 18).

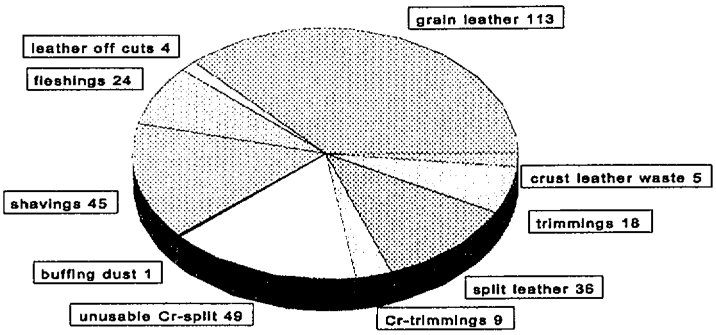


Figure 18. Collagen distribution in leather and solid waste - splitting in chrome
(kg/1 000 kg of wet salted hide)

Where the utilisation of collagen by-products is concerned, lime splitting is the superior technology.

5.2. Chrome

The basic mass balance of chrome is shown in Figure 8. When post-tanning operations are also considered, the analysis of chrome balance, as in the case of collagen, shows that in a tannery applying conventional technology even less than 50 percent of the Cr_2O_3 offer is retained in the leather (Figure 19). Using modern chrome tanning methods, such as high exhaustion, recycling or recovery, much higher chrome efficiency can be achieved.

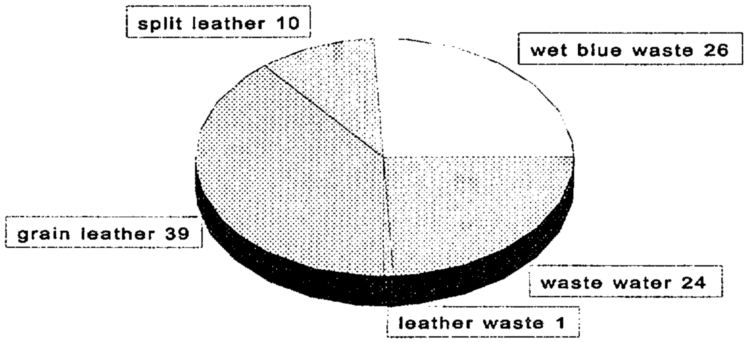


Figure 19. Chrome distribution in leather, solid waste and effluent
(expressed as % of Cr_2O_3 offer)

5.3. Water consumption

Water consumption, usually expressed in litres per kilogram or m^3/ton of wet salted weight, is also one of the main criteria when evaluating mass efficiency in a tannery. Today, water is seen as one of the chemicals needed for the process - and not as a commodity that is readily available. The cost of setting up and operating an effluent treatment plant is also directly related to water consumption.

Water consumption consists of two main components: **process water** (drum - float processes, vacuum drying, finishing, cleaning etc.) which, in our case, is estimated at approximately 32 m^3; and **technical water** needed for energy generation, waste water plant operations, sanitary purpose etc. which is estimated at 8 m^3, total 40 m^3/1,000 kg of wet salted hides. In technically advanced plants, consumption is considerably lower and figures below 25-30 m^3/ton are already quite common, recycling of water from vacuum dryers being one of the first measures.

The estimates of water consumption under the conditions assumed by this study are given in Figure 20.

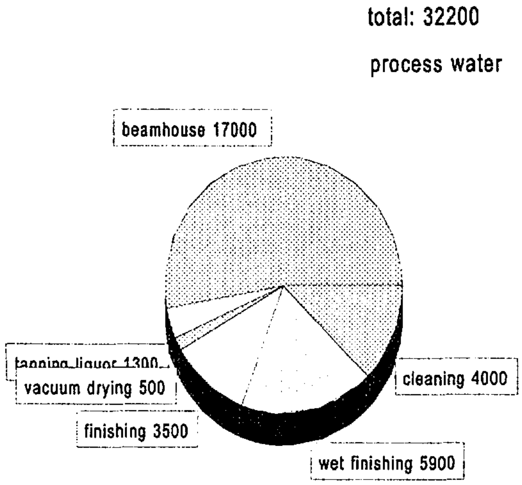


Figure 20. Water consumption in different stages of leather manufacturing
(litres/1,000 kg of wet salted hides)

5.4. Efficiency of utilisation of some other components

Estimates of efficiency derived from utilising other important materials, such as organic tannins, fat liquors and dyestuffs, together with those of collagen and chromium, are shown in Figure 21.

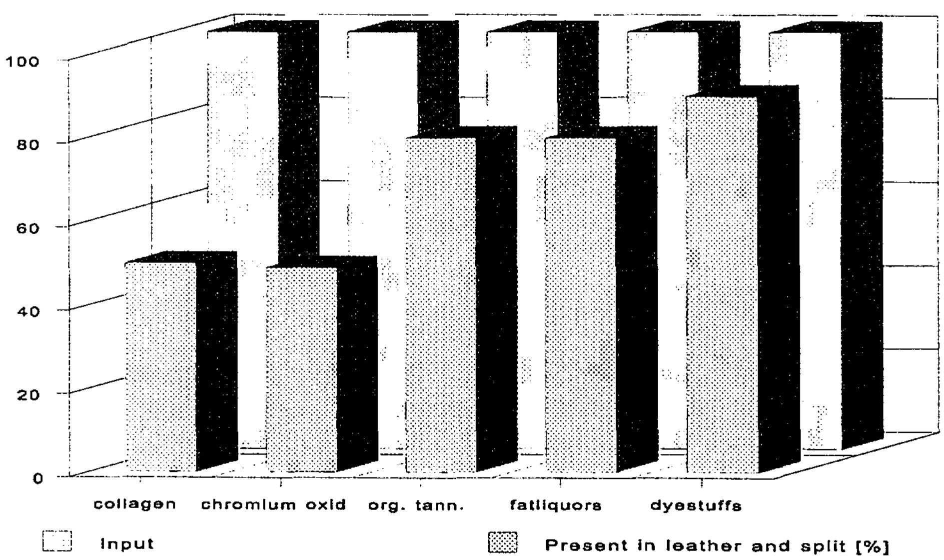


Figure 21. Mass efficiency of leather manufacturing
(Collagen, Cr_2O_3, organic tannins, fat liquors, dyestuffs)

It is estimated that out of 452 kg of process chemicals used only 72 kg are retained in and on leather and 380 kg are wasted and discharged in various forms. Thus, the effective utilisation of process chemicals is only about 15%, implying that the remaining 85% enter the waste streams.

5.5 Yield

a) In terms of weight

It is estimated that in the weight category described in the table of basic assumptions and using the process described in Annex 1, one ton (1,000 kg) of wet salted hides, average weight 28 kg/hide, would give 195 kg of grain and 60 kg of split: a total yield of 255 kg of finished leather.

b) In terms of area

It is estimated that one ton of raw hide (i.e. 39 hides, average area 4 m^2/hide,) with a total surface area of approximately 156 m^2 yields 138 m^2 of grain leather and 60 m^2 split (Figure 22). The yields related to green weight are as follows: grain leather 12.5 dm^2/kg and split leather 5.4 dm^2/kg: a total yield of 17.9 dm^2/kg green weight.

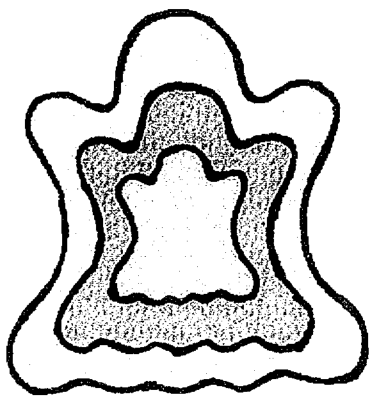


Figure 22. Area yield of grain leather and split leather
(green - raw hide, brown - grain leather, blue - split leather)

Fortunately, the mass balance of leather manufacturing can be improved in many different ways. It is always necessary, however, to know the starting-point. This study may help a tanner to analyse a specific situation in his plant and find optimal solutions to the problem of waste reduction.

5.6 Waste - pollution load generated

Efficiency measured in terms of the amount of pollutants generated has to be analysed and interpreted with great caution. Introduction of cleaner processing methods, such as hair saving, liming, CO_2 deliming, high exhaustion and recycling, leads to a lower total load but the decrease in water consumption results in a higher concentration of pollutants (ie higher values in mg/l). In extreme cases, it can lead to poor treatability of effluent. In our case, it is estimated that the pollution load generated would be as follows:

Suspended solids (SS)	116	
COD		188
BOD_5		68
Cr^{3+}		5
S^{2-}		7
NH_3-N	5	
TKN		15
Cl^-		170
SO_4^{2-}		81

Figure 24. The amount of pollutants generated - *kg/1,000 kg of wet salted hides processed*

Assuming a level of efficiency of sedimentation after primary (physico-chemical) treatment of 60 per cent, the amount of suspended solids removed is 116 x 0.6 = 70 kg of dry substance (DS) corresponding to approximately 1,750 kg of primary sludge at 4 per cent of DS content.

The total quantity of sludge (including biological treatment) dewatered to approximately 30 per cent of DS will be approximately 420 kg for one ton of wet salted hides.

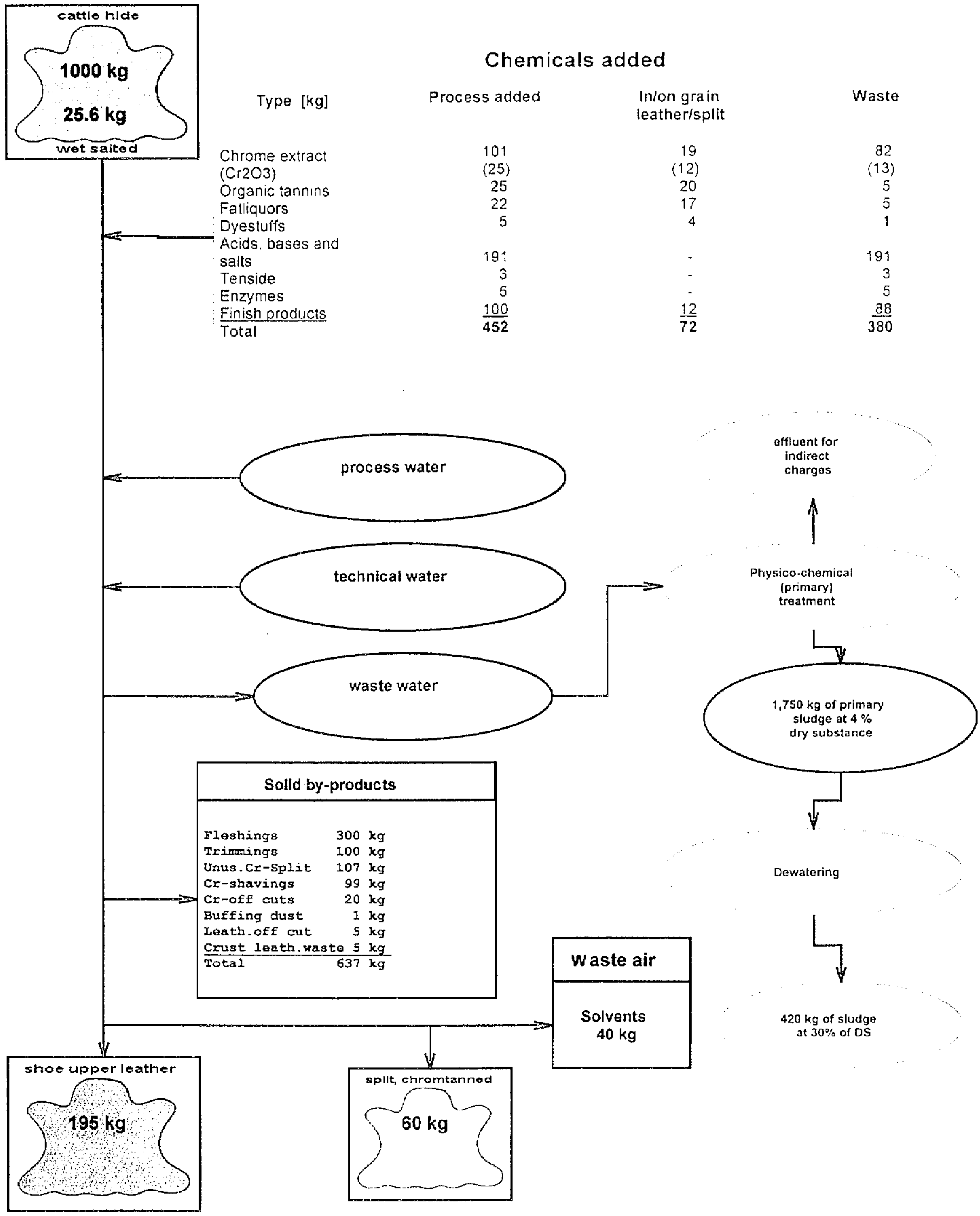


Figure 23. Mass balance in leather processing

REFERENCES

1. Hellinger, H. "Abfallvermeidung und -verwertung in der Lederindustrie, TV 3: Ökologische Gesamtbilanz der lederherstellenden Industrie" 15. 10. 1993, Research report FILK, Freiberg.

2. Rundschreiben Nr. 8/1992 des Verbandes der Deutschen Lederindustrie.

3. Herfeld, H. "Bibliothek des Leders", Umschau Verlag, Frankfurt, especially:
Vol.1, Herfeld, H. "Die tierische Haut", 1990.
Vol.2 Zissel, A."Arbeiten der Wasserwerkstatt bei derLederherstellung" 1989.
Vol.8 Feikes, L. "Ökologische Probleme der Lederindustrie", 1990.

4. Reich, G. "Stand und Tendenzen der Verwertung von Sekundärrohstoffen der Lederindustrie", Leder, Schuhe, Lederwaren, 19, (1984) p. 263-267

5. Reich, G. "Die festen Abfälle und Reststoffe der Lederwirtschaft - woher, wohin?", Das Leder 44, (1993) p. 161-171

6. Reich, G. "Verwertungsmöglichkeiten für chromgare Lederabfälle", Das Leder, 41, (1990) p. 217-222.

7. Vulliermet, B. "Improvement of the Mass and Energy Balances in the Tanning Industries" J. Amer. Leather Chem. Ass., 75, (1980) p. 233-275.

8. Alexander, K.T.W., Corning, D.R., Cory, N.J., Donohue, V. J. and Sykes R.L., "Environmental and safety issue - clean technology and environmental auditing", J. Soc. Leather Techn. Chem., 76, (1992) p. 17-23

9. BASF "Ecological Production" , Leather, March 1995 p.86-92

10. UNIDO Publication: "Acceptable Quality Standards in the Leather and Footwear Industry", 1996.

11. Hillion, I. "Ausbeutebilanz der Rohhaut", Das Leder, 33, (1982) p. 201-204

12. Radil, M. "Über die Erzeugung von Hautfasern bei der Erzeugung semisynthetischer Oberleder für die Schuhfertigung", Das Leder, 22, (1971) p. 251-255

13. Taschenbuch für den Lederfachmann , BASF, 1994.

14. Abwassertechnische Vereinigung (ATV), Germany: "Die Abwasserbehandlung in der Lederindustrie" (unpublished draft report 1995).

15. May, M.: "Automated production, plus logistic and eco-efficiency in tanning",15. 04. 1994.

16. Manzo, G.,Grasso, G.,Bufalo, G.: "Chrome tanning process with "integrated recycle" modeling, flow chart, design and mass balance", Proceedings XXIII. IULTCS-Congress, Friedrichshafen 1995, Vol. 2, Poster 79

17. Frendrup, W.: "UNEP cleaner production industrial sector guide leather industry", 1996.

18. Püntener, A. "The ecological challenge of produce leather"J. Amer. Leather Chem. Ass., 90, (1995), p. 206-219

19. Püntener, A. "Ökologie und moderne Lederherstellung", Leder und Häutemarkt, 47, (1995), p. 276-286

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Annex 1

FORMULATION USED AS A BASIS FOR COMPUTATION OF MASS BALANCE

Shoe upper leather (grain and split leather)

BEAMHOUSE			
Basis: salt weight, 1000 kg			
Presoaking	150%	H_2O	1.5 m^3
	0.15%	tenside	1.5 kg
Main soaking	150%	H_2O	1.5 m^3
	0.15%	tenside	1.5 kg
Liming	200%	H_2O	2 m^3
	2.5%	Na_2S (60%)	15 kg (dry)
	1.5%	NaHS(70%)	10 kg (dry)
	4%	$Ca(OH)_2$	40 kg
Washing	300%	H_2O	3 m^3
Fleshing, trimming			
Washing	400%	H_2O	4 m^3
Basis: pelt weight, 1100kg (unsplit)			
Deliming, bating	200%	H_2O	2 m^3
	2.5%	ammonium salts	27 kg
	0.8%	weak acids	9 kg
	0.5%	enzyme products	5 kg
Washing	300%	H_2O	3 m^3
Basis: pelt weight, 750 kg (ex-lime grain split)			
Deliming, bating	200%	H_2O	1.5 m^3
	2.0%	ammonium salts	15 kg
	0.4 %	enzyme products	3 kg
Washing	300%	H_2O	2.2 m^3

Basis: pelt weight, 195 kg (ex-lime flesh split)			
Deliming, bating	200%	H_2O	0.4 m^3
	1.0%	ammonium salts	2 kg
	0.2%	Enzyme products	0.4 kg
Washing	300%	H_2O	0.6 m^3
TANNING			
Basis: pelt weight, 1100 kg (unsplit)			
Pickling	50%	H_2O	0.55 m^3
	5%	NaCl	55 kg
	1%	acids	11 kg
Tanning	70%	H_2O	0.75 m^3
	8%	basic chrome sulphate (25% Cr_2O_3)	88 kg
	0.7%	Basic agent Na_2CO_3 or MgO	8 kg
sammying, splitting, trimming, shaving			
POST TANNING Wet Work - Grain Leather			
Basis: shaved weight 262 kg			
Washing	400%	H_2O	1 m^3
Neutralisation	200%	H_2O	0.5 m^3
	1.5%	$NaHCO_3$	4 kg
	1.5%	HCOONa	4 kg
Washing	400%	H_2O	1 m^3
Retanning, dyeing, fatliquoring	100%	H_2O	0.3 m^3
	5%	basic chrome sulphate (25% Cr_2O_3)	13 kg
	10%	organic tannins (75%)	20 kg
	8%	fatliquor (70%)	15 kg

	2%	dyestuffs (75%)	4 kg
	1.5%	Acids	4 kg
Washing	600%	H_2O	1.6 m^3
vacuum drying			
POST TANNING Wet Work- Splits			
Basis: shaved weight, 88 kg			
Washing	400%	H_2O	0.35 m^3
Neutralisation	200%	H_2O	0.2 m^3
	1.5%	Na_2CO_3	1.3 kg
	1.5%	HCOONa	1.3 kg
Washing	400%	H_2O	0.35 m^3
Retanning, fatliquoring, dyeing	100%	H_2O	0.1 m^3
	8%	organic tannins (75%)	5.3 kg
	10%	fatliquor (70%)	6.2. kg
	2%	dyestuffs(75%)	1.3 kg
	1.5%	acids	1.3 kg
Washing	600%	H_2O	0.5 m^3
vacuum drying			
FINISHING: The mass balance for finishing has been calculated on the basis of leather area; the composition of coatings applied expressed as dry substance			
a) Grain (crust) leather, lightly corrected, 141 m5			
Impregnation (curtain coating):			
250 g/m5, dry matter content 10%		Applied	On leather
	finish	35.0 kg	-
	solids	3.5 kg	3.5 kg
Base coat (reverse roller):			
1 x 100 g/m5, dry matter content 25%	15 % loss		

1 x 80 g/m5, dry matter content 25%		15% loss	
	finish	25.0 kg	-
	solids	6.5 kg	5.5 kg
Top spray (rotary sprayer):			
100 g/m5, dry matter content 6%		40% loss	-
	finish	14.0 kg	-
	solids	0.9 kg	0.5 kg
b) Split (crust) leather 61m5			
Base coat (reverse roller):			
1 x 250 g/m5, dry matter content 10%		15% loss	-
1 x 80 g/m5, dry matter content 10%		15% loss	-
	finish	20.0 kg	-
	solids	2.0 kg	1.7 kg
Top spray (rotary sprayer):			
100 g/m5, dry matter content 20%		40% loss	-
	finish	6.0 kg	-
	solids	1.0 kg	0.6 kg

ANNEX 2

Salt preservation, relationship green/salt weight

Although hides are not cured in a tannery, the manner of their preservation has a direct impact on mass balance and the quality of effluent. In the most frequently applied method of preservation (i.e. with common salt), the dosage is usually approximately 40% of salt (NaCl) calculated to the raw hide ('green') weight. Owing to dewatering and the loss of soluble organic substances such as soluble proteins (albumin), dung, dirt and blood on the one hand and the absorption of salt by hides on the other, conversion from fresh ('green') into 'wet salted' state results in a loss in weight as shown in Figure 1.

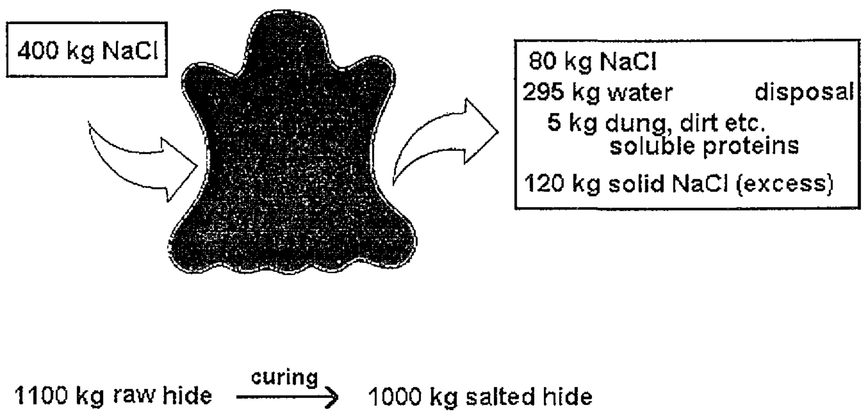

Figure 1. Mass balance and weight changes caused by curing with common salt

The environmental significance of hide curing with salt can be seen from the 'salt balance' (Figure 2) prepared for hide production in Germany in 1992 (Ref.1). It conforms quite well with proportions given in Figure 1.

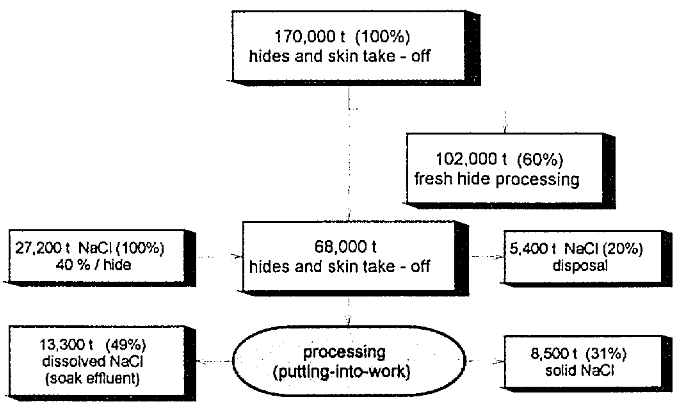

Figure 2. "Salt balance" of hide production in Germany in 1992 (Ref. 1)

Disregarding some (sub)components of lesser importance (e. g. % fat, soluble hide components like different proteins, proteo-glycanes etc.) and focusing on the three key components mentioned earlier (**corium:** contains collagen the real leather-building substance: **epidermis:** mainly hair, cells and some protein-like substances removed by liming: and **subcutis:** collagen and some other proteins as well as fats that are removed by fleshing during the beamhouse processes), the changes in hide composition occurring during salt curing are shown in both relative and absolute terms: Figure 3A (%) and Figure 3B (kg

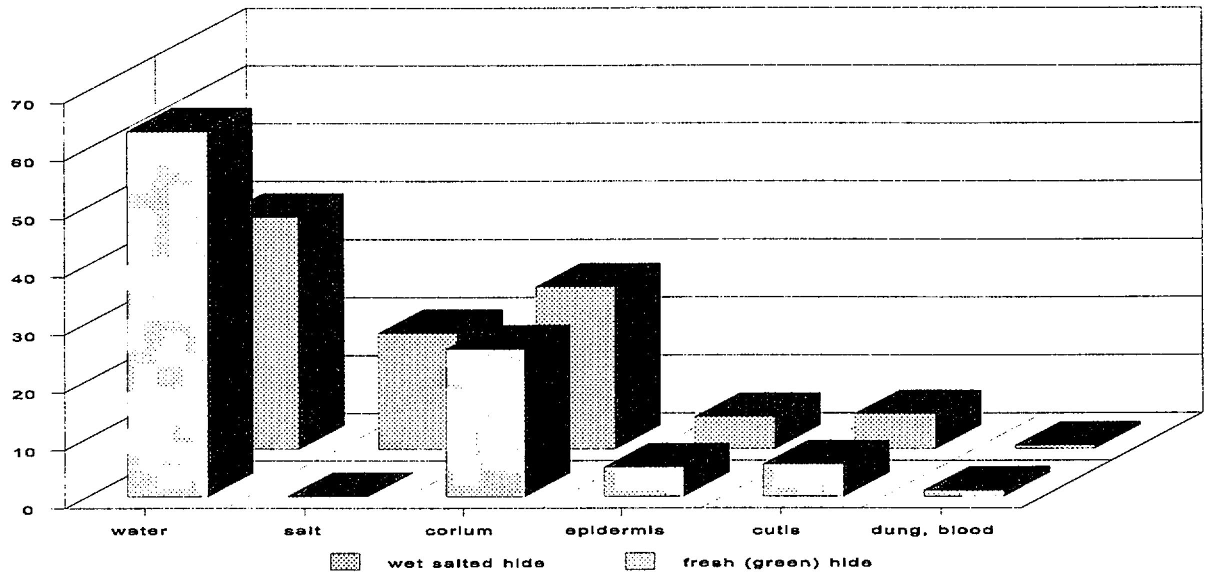

Figure 3A. Changes in hides composition during salt curing - percentage of share

Components	Fresh (green) hides	Wet salted hides
	kg	kg
Water	690	400
Salt	0	200
Corium	280	280
Epidermis	55	55
Subcutis	60	60
Proteins, dirt, etc.	15	5
TOTAL	**1100**	**1000**

Figure 3B. Changes in hides composition during salt curing - absolute values

These figures clearly emphasise the need to find alternatives: processing fresh hides, wherever practicable, is certainly the best alternative