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MASS BALANCE IN LEATHER PROCESSING

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CONTENTS

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 shopfloor 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.

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:

- C **Corium:** collagen containing the true "leather-building substance"
- C **Epidermis:** mainly hair, cells and certain protein-like substances that are removed through liming
- C **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 $_2$ S is oxidized. Certain - almost negligible - amounts of NH $_3$ and H $_2$ S 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.

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.

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:

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 | | | | |
| Bi-nuclear complex | | | | | 10 | |
| Cr_2O_3 | ⌒ | 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).

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).

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

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).

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).

Figure 15. Mass balance: Finishing of grain leather (*in kg*/141 m² crust grain leather)

Finished embossed split

Split leather

Figure 16. Mass balance: Finishing of split leather (*in kg/61 m² 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.

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 Cr2O3 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 m³; and **technical water** needed for energy generation, waste water plant operations, sanitary purpose etc. which is estimated at 8 \overrightarrow{m} , total 40 $\overrightarrow{m'}$ 1,000 kg of wet salted hides. In technically advanced plants, consumption is considerably lower and figures below 25-30 m³/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, Cr2O3, 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/h ide,) with a total surface area of approximately 156 m² yields 138 m² of grain leather and 60 m² 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, $CO₂$ 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:

| 116 | |
|-----|-----|
| | 188 |
| | 68 |
| | 5 |
| | |
| 5 | |
| | 15 |
| | 170 |
| | |
| | |

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 $116 \times 0.6 = 70$ 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.

cattle hide

Figure 23. Mass balance in leather processing

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FORMULATION USED AS A BASIS FOR COMPUTATION OF MASS BALANCE

Shoe upper leather (grain and split leather)

 H

