Umweltbundesamt
IV 2.2 - 97356/1
responsible: Doris Schubert
Email: doris.schubert@uba.de

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IC-07 Leather Processing Industry

Assessment of the environmental release of chemicals from the leather processing industry

(revised version of 28 July 1998)

Contents

1. Introduction

This document provides realistic worst case release scenarios for chemicals used in the production and finishing of leather (IC-07; UC-10, 51, ...). These guidelines enable estimates of concentrations of substances in waste water emitted from sites where these activities are carried out:

- for releases by syntheses of chemicals used in the leather industry, see specific scenario for production.
- for releases by their formulation, see IC-07 tables A and B.
- for releases into the environmental compartments "air" and "soil" at all stage of life cycle see IC-07, tables A and B.

Leather is produced from skins of different types of wild and domestic animals. The structure of the skin is based on interlaced bundles of micelles and fibrils, the collagen. Respectively, three peptide-chains form a triple alpha-helix structure. Five of them form microfibril units which in turn form higher fibric structures. These structures are stabilised internally and laterally (cross linked) by hydrogen-bonds between the peptide groups of the amino acids. In the tanning process the hydrogen-bonds are replaced by substances like chromium sulphate, alum or vegetable tanning agents.

Leather production belongs to the natural product industry. It comprises:

- tanning of the skin to stabilise the material against microbial protolytic enzymes in the wet environment, prevention of fracture in the dry environment and of gluing in hot surrounding.
- giving properties and fashion effects to the leather which are requested by the market.

Production of leather goods is characterised by intermittent mechanical and chemical (batch) treatments, often high in number. Depending on the desired type of the final product the hides undergo a wide variety of processing steps. The waste waters arising from the individual steps are sometimes separately pre-treated, but in most cases are mixed before discharge in order to make use both of dilution and neutralisation effects.

2. Main processes

Beamhouse operations, tanyard operations, dressing operations and finishing operations are components of the leather production. Both, the high variability of the raw materials and the different properties of the final product require a high number of differing processes which can be summarised as follows.

Beamhouse operations

- ***Wetting and soaking:*** The initial water content of the untanned leather is adjusted, mainly by a two-stage cleaning of the skin, preliminary and main soaking. This brings about extraction of water-soluble peptides and emulgation and saponification of lipids. These processes may be accelerated by adding protolytic or lipolytic enzymes.
- ***Liming:*** Removal of the upper epidermis layers, including hairs etc. in a bath of calcium hydroxide and sodium sulfide. This results in decomposition and swelling of the skin by the reduction of S-containing amino acid of the keratin fraction and by hydrolysis of pre-

keratins in the basal epidermis layer; widening the polypeptide layers for further tanning treatment.

Tanyard operations

- ***Deliming:*** The treated untanned leather is neutralised by mild acidic compounds like formic acid, lactic acid, boric acid etc. and their salts. The lime is transferred to soluble Ca-salts.
- ***Degreasing:*** Fat is removed by emulsifiers (anionic, cationic, non-ionic) or by organic solvents. This step is mainly used for sheepskin
- ***Pickling:*** Further loosening of the skin and preparation for tanning solutions is achieved in a solution containing salts and acids (HCl, H_2SO_4, organic acids, NaCl). The carboxyl groups of the skin (amino acids) are blocked by the acids, in order to give the small tanning agent molecules the possibility of penetrating in to deeper layers of the skin.
- ***Tanning:*** In most cases chromium (III) salts, sometimes additionally aluminium and zirconium salts are used as tanning agents. After the small sized molecules of the tanning agent have penetrated the material alkali (mainly soda) is added. Increasing the pH leads to formation of larger sized complexes. Binding is achieved by ligand exchange of the carboxyl functions of the protein which have a higher affinity than the ligands of the mineral complex. The result of this processing step is called "wet-blue" leather. Second tanning steps are necessary for specific leather properties.

Dressing operations

- ***Washing:*** After the tanning process the leather is washed. While washing waters from tanning contain high salt concentrations from neutralisation steps, tanning agents can also be found.
- ***Dyeing, fatliquoring:*** In most cases dyeing is performed to gain the desired colour of the material and fatliquoring is employed to keep the material's smoothness, toughness and elasticity. This is achieved by adding lubricating fats (natural or synthetic) which allow slipping of the leather fibres and thus avoid destruction of the material from mechanical (bending) stress. The result of this processing step is called „crust“ leather.

Finishing operations

- ***Finishing:*** Grain leather is generally surface treated by the addition of lacquor and/or resin containing colorants and other additives in either aqueous or organic solvent systems. Leather products typically need several coatings (base coat(s), effect coat, top coat(s)). They contain pigments and/or metal-complex dyes in dispersion matrices consisting of polyurethane and other polymers, waxes, collodium etc. Suede leather is not generally finished.

3. Main chemicals used

The quantities of chemicals used at each stage, per ton of salted wet hide, may be grouped together as indicated in the table 1.

Table 1 *Quantities of the main chemicals (C.T.C, France, 1997)*

Process	***Chemical***	***Maximum quantity per ton of salted wet hide***	
		[%]	[kg]
Curing	Sodium chloride	30.0	300
	Antiseptics	0.3	3
Beamhouse	Wetting agents	0.3	3
	Antiseptics	0.2	2
	Sodium sulphide	4.0	40
	sodium hydrosulfide	2.0	20
	Slaked lime	5.0	50
	Caustic soda	2.0	20
	Sodium carbonate	3.0	30
	Enzymes	1.5	15
	Mercaptans	4.0	40
	Ammonium chloride	2.0	20
	Ammonium sulfate	2.0	20
	Organic acids	2.0	20
Tanning	Sodium chloride	10.0	100
	Sulfuric acid	3.0	30
	Formic acid	2.0	20
	Organic solvents	16.0	160
	Wetting agents	4.0	40
	Sodium carbonate	2.0	20
	Chromium salts	10.0	100
	Sodium bicarbonate	1.0	10
	Vegetable tans	30.0	300
	Glutaraldehyde	2.0	20
Dressing	Neutralising agents	2.0	20
	Retanning agents	4.0	40
	Dyes	4.0	40
	Fat-liquoring oils	12.0	120
Finishing	Finishing agents	4.0	40

4. Release Estimation

Information on the structure and representative production- and finishing volumes of the leather industry of the EU is incomplete.

In a research project „Abwassereinleiter-Statistik“ (waste water statistics) initiated by the German Federal Environmental Agency (UBA in 1997) a survey of the German leather

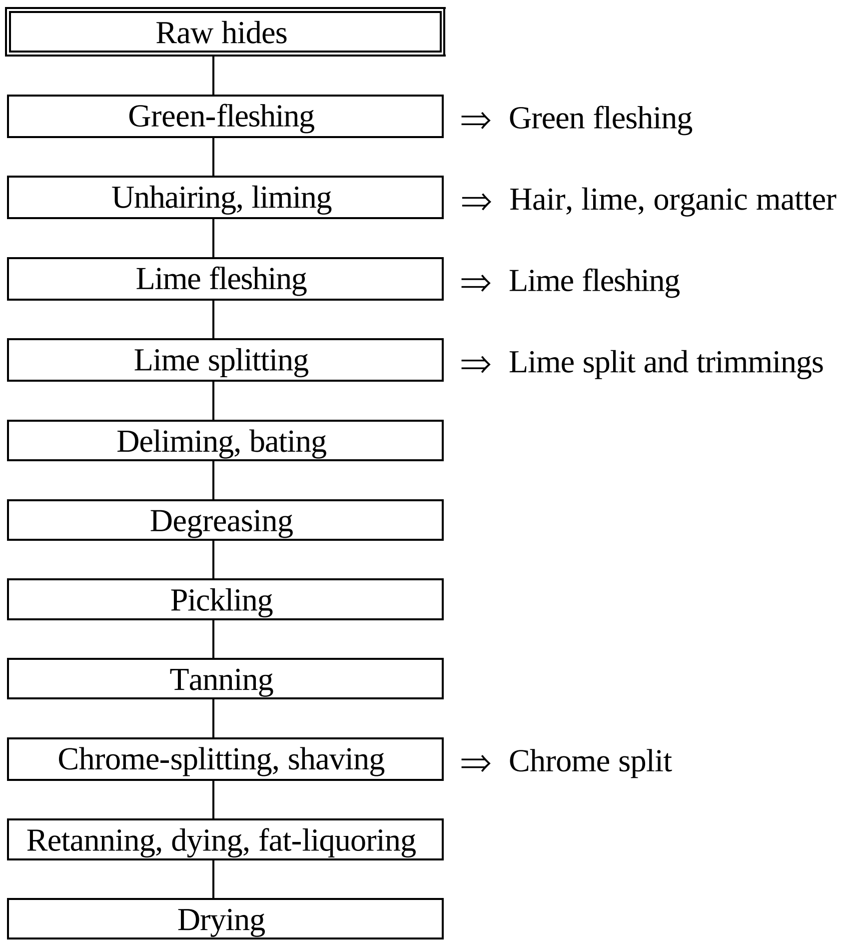
processing industry and a statistical evaluation of different branch and process specific values were performed.
The statistical result was, that the mass processed per day for a representative firm in Germany with the EU-standard waste water treatment flow rate EFFLUENTstp= 2000 m³/day and the EU-standard DILUTION factor of 10 is **15 t rawhide per day**.
The mass per day for a representative „wet-blue processing“ company in Germany with EFFLUENTstp = 2000 m³/day and DILUTION = 10 is **3.2 t finished leather per day**.

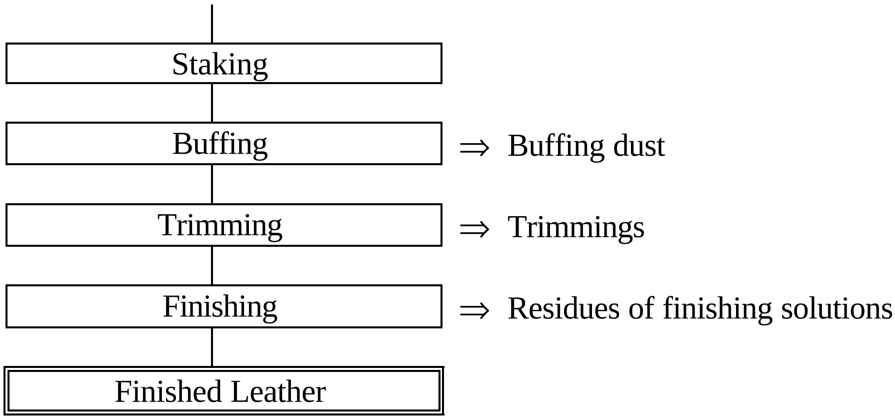
On the assumption that 1 t raw skin results 0.1 to 0.28 t crust leather (leather before finishing) it can be concluded that for 3.2 t finished leather approximately 10 to 30 tons of raw hide processed. This value is dependent on the kind of finished leather, e. g. leather for furniture, shoes and gloves.
For the parameter „mass of processed goods per day“ (W1) in the release estimation should be used 15 t raw hide per day.
Note: The parameter „mass of the substance used per mass of good“ (W2) must be also related to rawhide.

4.1 Solid waste

Solid waste comes mainly from leather production process. It is assumed, that 600 - 1000 kg of solid waste results per ton of processed raw hide or skin.

Diagram 1 *General outline of leather production -- solid waste* (C.T.C, France, 1997)





Solid waste arises also from used leather products. The major part of this material (shoes, clothes) ends up in the domestic waste streams and is disposed of in landfills or is incinerated. In general, exposure concentrations from products of the leather industry cannot be contributed to a high number of diffusive sources.

4.2 Branch specific values

4.2.1 Waste water amount

Depending on the capacity of the plants, technology of tanning, dyeing etc. and waste water management, volumes of effluent and concentration of ingredients varies within large ranges. Nevertheless, the effluents arising from different processing steps show characteristic composition.
For those plants which integrate all stages from processing of raw skins to final leather at one production site a typical water consumption rate (median) is 21 m^3 per ton of rawhide. Such plants specialised on processing (refining) of wet blue operate at a base of about 25 m^3 per ton of finished leather. The median waste water amount of the total branch is 56 m^3 per ton finished leather. (UBA Research project „Abwassereinleiter-Statistik“, Germany, 1997). Although the amount of waste water is not considered when evaluating the release of substance according the mass flow approach.

The individual stages of soaking, liming, deliming, pickling and tanning may be summarised as "beamhouse tanning". The outcome of wet processes is "wet blue" material. Detailed figures about averaged water consumption are provided by table 2.

Table 2 *Averaged water consumption and characteristics of waste water from chrome leather production and finishing.(according UBA Research project „Abwassereinleiter-Statistik", Germany, 1997)*

Process		***m³/t rawhide*** *Hellinger, 1993*	*Warner, 1992*
Beamhouse	soaking liming deliming and bating	6 9 5	6 9 5
	sum	**20**	**20**
Tanning	pickling and chrome tannery washing after chrome tannery	2,5	4
	sum	**2,5**	**4**
Sammying water out		**0,5**	
Wet finishing (grain leather)	washing, neutralisation, washing after neutralisation retanning, dying, fatliquoring washing dressing, cleaning	6,3 2,5 0,2	7,5 5,5 27
	sum	**9**	**40**
Sprayfinishing			
total amount of waste water		***32***	***64***

Local water authorities are responsible for stipulating and monitoring limits of pH, maximum content of organic material and standards for content of specific metals (e.g. Cr^{3+}) in waste water effluents. Cr^{3+} is mainly coming from the tanning process. For these reason pre-treatment of waste water is common practice. This leads also to a partial removal of substances (e.g. dyes) from the aqueous phase by precipitation.

There are two main sources of release of colorants or processing chemicals from leather tanneries:

- washings from cleaning or disposing of shipping containers, machinery etc.
- unused active substances in spent baths.

4.2.2 Production and processing per day

The median of processed mass in complete processing sites is 16 tons of raw skins per day (arithmetical mean: 27 t raw skins per day). The median of produced mass by wet-blue processors is 0.8 tons finished leather per day (arithmetical mean: 2.4 t per day).
(UBA Research project „Abwassereinleiter-Statistik", Germany, 1997)
Processing of 1000 kg raw skin results in 250 to 600 kg wet blue. A lot of plants are specialised on post tanning (second tanning, dyeing, stuffing) of wet blue material.

4.2.3 Number of working days

The median of number of working days in the same branch in 1995 is 220 days per year (arithmetical mean: 224 days per year).
(UBA Research project „Abwassereinleiter-Statistik“, Germany, 1997)

4.3 Leather dyeing

The dominant source of dye released from leather tanneries is the draining of used dyebath solutions. Acid dyes (which account for about 90 % of the market), metal complex dyes and, to a lesser extent, cationic dyes are applied as leather colorants either on the grain or suede side. Two types of dyeing methods are in use:

- drum dyeing (dominant)
- rub dyeing.

Using general estimates for parameters such as type of dyeing, liquor ratio and equilibrium constant the following estimates for degrees of fixation (*F*), respectively, are given in table 3.

Table 3 *Estimated degree of fixation for different types of dyes (ETAD, 1992)*

type of dye	degree of fixation (*F*) (average) in [%]	range in[%]
sulphur	70	65 - 95
metal complex	94	82 - 98
acid dye	100	98 - 100
unknown/acid groups	96	84 - 99

Table 4 shows, that 9 % of the sites dyeing the total production per day with one dyestuff. On the average 73 % of the sites dyeing less than half of production per day with one dyestuff. Therefore the default „participation factor on production per day“ [A] should be **50 %.**

Table 4 *Participation on dyed production per day with main dyestuff (UBA Research project „Abwassereinleiter-Statistik“, Germany, 1997)*

Average part of main dye per day	Sites
0 %	**5 %**
>0 - 20 %	**41 %**
>20 - 50 %	**27 %**
>50 - 99 %	18 %
100 %	**9 %**

It should be kept in mind that the mass of dye used per mass of good (W2) is referring to the weight of rawhides because the proposed representative processing volume of 15 tons per day is also related of rawhide. If no specific data are available, the coloration should be assumed as 1 % (10 kg dyestuff formulation for 1 ton of rawhide). If the content of dyestuff in the formulation are not available, it should be assumed as 100 %.

The release during one working day may be calculated using the equation:

$$E = W1 \times W2 \times \frac{(100 - F)}{100} \times \frac{A}{100} \qquad (1)$$

Explanation of symbols:		Dimension	Default
E	emission per day	[kg/d]	
W1	mass of dyed good (raw hide) per day	[t/day]	15
W2	mass of dye used per mass of good (raw hide)	[kg/t]	10
F	proportion of substance fixed to the substrate	[%]	see table 3
A	participation factor on production per day	[%]	50 %

4.4 Leather processing, other than dyeing (tanning, pickling etc.)

The release during one working day may be calculated using the equation:

$$E = W1 \times W2 \times \frac{(100 - F)}{100} \qquad (2)$$

Explanation of symbols:		Dimension	Default
E	Emission per day	[kg/d]	
W1	mass of processed good (raw hide) per day	[t/day]	15
W2	mass of the substance used per mass of good (raw hide) (information from notifier)	[kg/t]	
F	degree of consumption (information from notifier) The proportion of the substance of interest charged which is chemically converted or fixed to good during processing.	[%]	

5. Example:

For a metal complex dye where:

W1 = 15 [t/d]
W2 = 10 [kg/t rawhide]
F = 98 [%]), (default: see table 3)
A = 50 [%]

E = 3 kg/d

5. References

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Calculation of PEC_{local} for aquatic compartment by leather production industry

status: TGD, ESD, IC-7

chemical :

$d := 86400 s$

$a := 365 \cdot d$

$\mu g := 10^{-9} \cdot kg$

Mass of processed goods per day: $W1 := 15 \cdot t \cdot d^{-1}$

mass of substance used per mass of good per t rawhide: $W2 := 10 \cdot kg \cdot t^{-1}$

Degree of fixation (tab. 2 / from notifier) $F := 95 \cdot \%$

Participation factor on production per day $A := 50 \cdot \%$

Waste water flow of wwtp: $EFFLUENT_{stp} := 2000 m^3 \cdot d^{-1}$

Fraction of emission directed to water: (SimpleTreat; k: h-1; logPow: ;logH:) $Fstp_{water} := 100 \%$

Dilution factor (TGD): $DILUTION := 10$

Factor (1+Kp*SUSPwater): $FACTOR := 1$

Emission per day:

$Elocal_{water\_a} := W1 \cdot W2 \cdot (1 - F) \cdot A$ $\qquad Elocal_{water\_a} = 3.75 \cdot kg \cdot d^{-1}$

Influent concentration:

$Clocal_{inf\_a} := \frac{Elocal_{water\_a}}{EFFLUENT_{stp}}$ $\qquad Clocal_{inf\_a} = 1.87 \cdot mg \cdot l^{-1}$

Effluent concentration:

$Clocal_{eff\_a} := Clocal_{inf\_a} \cdot Fstp_{water}$ $\qquad Clocal_{eff\_a} = 1.87 \cdot mg \cdot l^{-1}$

Concentration in surface water:

$Clocal_{water\_a} := \frac{Clocal_{eff\_a}}{DILUTION \cdot FACTOR}$ $\qquad Clocal_{water\_a} = 187.5 \cdot \mu g \cdot l^{-1}$

$Clocal_{water} = PEC_{local}$ for $PEC_{regional} = 0$