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EMISSION SCENARIO DOCUMENT ON LEATHER PROCESSING

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Series on Emission Scenario Documents No. 8

EMISSION SCENARIO DOCUMENT ON LEATHER PROCESSING INDUSTRY

Environment Directorate

Organisation for Economic Co-operation and Development

June 2004

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The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 30 industrialised countries in North America, Europe and the Pacific, as well as the European Commission, meet to co-ordinate and harmonize policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised Committees and subsidiary groups composed of Member country delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's Workshops and other meetings. Committees and subsidiary groups are served by the OECD Secretariat, located in Paris, France, which is organised into Directorates and Divisions.

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The Environmental Health and Safety Programme co-operates closely with other international organisations. This document was produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organization Programme for the Sound Management of Chemicals (IOMC) was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and the OECD (the Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. UNITAR joined the IOMC in 1997 to become the seventh Participating Organization. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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or contact:

**OECD Environment Directorate,
Environmental Health and Safety Division**

**2 rue André-Pascal
75775 Paris Cedex 16
France**

Fax: (33-1) 45 24 16 75

E-mail: ehscont@oecd.org

Explanatory notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, production processes, pathways and use patterns of chemicals used as additives in plastics to assist in the estimation of releases of chemicals to the environment.

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other that the lead (Germany). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The submitted information will also be made available to users within the OECD web-site (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

The following data and information should be available for the estimation of the emissions of chemicals used in leather processing:

- intended use of chemical (e. g. dyestuff, biocide)
- step of process
- concentration in preparations

Coverage

This ESD covers the Industry Category 7 – leather processing industry. It describes the processes of the life cycle stage "industrial use" and the emission estimations to local surface waters. The stages "service life of article" and "disposal" are not covered and need to be added at a later date.

How this document was developed

This document is based on the ESD for Industry Category 7 "Leather Processing Industry" published in the "Technical Guidance Document (TGD) on risk assessment in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No 1488/94 on risk assessment for existing substances", Part IV Chapter 7 (EU, 1996). In the years 1996-1997 Umweltbundesamt (UBA, Germany) commissioned research on effluents from the leather processing industry in Germany and obtained statistical data on this industry sector (Böhm et al. 1997, 2000; Hillenbrand et al. 1999). These data were used to revise the generic point source. Then, in the years 2000-2001 Umweltbundesamt and the Institut National de l'Environnement Industriel et des Risques (INERIS), France, jointly updated this document and incorporated biocides in the context of the European EUBEES project. This document was published in 2003 by the European Commission in the updated Technical Guidance Document for Risk Assessment (EU, 2003).

Germany as a lead country submitted this draft to OECD, and the draft was circulated to the member countries in February 2002. Comments were received from the following organizations, institutions, and persons: UK (Environment Agency and Health and Safety Executive), US EPA, German, UK and US industries, and Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers (ETAD) (OECD, 2002).

In 2003 Umweltbundesamt commissioned Christiane Hauber of the Lederinstitut Gerberschule in Reutlingen, Germany (Leather Institute and Tanners' School)

- to incorporate the comments and to revise the draft accordingly,
- to harmonize the document with the BREF Document on Best Available Techniques for the Tanning of Hides and Skins. Integrated Pollution Prevention and Control. European IPPC Bureau, Sevilla/Spain, May 2001 (BREF 2003),
- to correct and to complete the description of processes in leather industry,
- to improve the homogeneity of the document, esp. concerning biocides.

On 11 September 2003 representatives from a leather chemical producing company (BASF), the German Association of leather chemicals producing companies (TEWEGA), the Association of the German Leather Industry (VdL), Umweltbundesamt and Christiane Hauber met in Frankfurt and examined the whole document. Agreed amendments and changes were introduced in Table 4.

TABLE OF CONTENTS

1. INTRODUCTION

1. This document provides realistic worst case release scenarios for industrial chemicals and biocides used in the production and finishing of leather (EU-industry cathegory-07, and biocidal product type 9). These scenarios enable estimates of local releases emitted from sites to wastewater where these activities are carried out.

2. Leather is produced mainly from hides and skins (for definitions see Glossary) of cattle, sheep, goat, pig, buffalo, and reptiles. Tanning is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather.

3. Fresh hides and skins consist of water, protein, fats, and some mineral salts. Of these, the most important one for leather making is the protein collagen. The skin consists of a network of collagen fibres composed of bundles of smaller fibrils, which consist of bundles of sub-microscopic micelles. These are made up of very long molecules of collagen twisted together. These structures are stabilised internally and laterally (cross linked) by hydrogen bonds between the peptide groups of amino acids. All mammal skins follow this basic pattern, but vary in size, shape, and thickness.

4. Tanning means converting the rawhide or skin, a highly putrescible material, into leather, a stable material. In this process the very sensitive hydrogen bonds are replaced by chemical bonds with tanning agents like chromium, aluminium or other mineral salts, vegetable or synthetic tanning agents to stabilise the material and to protect it against microbial attack. Leather production belongs to the natural products industry. The whole process involves a sequence of complex chemical reactions and mechanical processes.

5. The production processes in a tannery can be split into four main categories:

- Hide and skin storage and beamhouse operations, in which the raw material is prepared for tanning.
- Tanyard operations, in which the raw material is tanned (stabilised).
- Post-tanning operations, in which the leather is re-tanned, dyed, and fatliquored giving properties and fashion effects to the leather depending on the demands of the market.
- Finishing operations include several mechanical treatments as well as the application of a surface coat.

6. Operations carried out in the beamhouse, the tanyard, and the post-tanning area are often referred to wet processes, as they are carried out in vessels (drums) filled with water or other liquids (fatliquoring). The finishing is referred to dry processing. Depending on the circumstances and the final products, the desired leather type, different options for the process will be applied and consequently different environmental impacts may occur.

7. Tanneries employ abatement techniques for the treatment of wastewater, waste, and air emissions generated during these processes. Tannery effluents have to be treated before they can be discharged to surface water. The wastewater treatment strategies vary, but in general mechanical pre-treatment, physico-chemical treatment, and biological treatment are involved on- or off-site (see chap. 5.8).

8. The European leather processing industry is present on the Internet with the following statistical data (Table 1).

Table 1 European leather processing industry in 2000 (Cotance 2000, BREF 2003)

Country	Employment [-]	Companies [-]	Turnover [10³ Euro]	Export [%]	Production [1000 m²]		Disposal route for sludge (1) [%]
					cattle, calf	sheep, goat	
Belgium	169	4	35667	73	349	836	L: 66 (2) I: 17 A: 17
Denmark	150	1	20000	85	725		
France	2583	84	325000	42	6000	4150	I: 95 A: 5
Germany	3211	27	546000	48	16000	incl. cattle	L: 100
Greece	n.a.						
Italy	30300	2400	6300800	59	168300	46550	L: 100
Ireland	400	2	40000	100	4080	67	L: 60 A: 40
Netherlands	600	20	n.a.				L: 100
Spain	7399	223	1288570	39	28300	20850	L: 90 A: 10
Portugal	1835	26	253219	18.8	9593	1288	
UK	3400	43	580000	63	11500	3200	L: 90 A: 10
Sweden	430	4	68500	85	2600		L: 100
Finland	229	16	28214	42	626	127	
Austria	1800	6					
EU-15	52506	2856	9485970	59.5	248087	77068	
Norway	160	3	25000	90	6000	40	L: 100
Switzerland	n.a.						
Hungary	n.a.						
Slovenia	590	7	105058	79.6	64	179	

n.a. = not available

(1) Sludge from wastewater treatment plants / sewage treatment plants; quoted from BREF (2003).

(2) L = landfill, I = incineration, A = agriculture.

9. The most important producer and transformer in Europe is Italy (84% of all companies), followed by Spain.

2. MAIN PROCESSES

10. The four main steps in processing hides and skins are:

- Hide and skin storage and beamhouse operations
- Tanyard operations
- Post-tanning operations
- Finishing operations

(for details see also BASF 2004)

Table 2 Main processes and releases of the tanning industry

Process	Stage at the end of the process	Hides and Skins	Main components in wastewater	Solid waste	Sludge
Beamhouse	Raw hide	Preliminary soaking and soaking	salt, tensides, organic N, bactericides		Sludge
		Green fleshing		Green fleshings	
Beamhouse	Pelt	Unhairing and Liming	organic N, lime, sulphide	Fleshing Lime split	Sludge
		Deliming and Bating	organic and inorganic N		
Tanning	Wet blue Wet white	Pickling and Chrome tanning or non-chrome tanning	acids, salt, chrome sulphate, fungicides		Sludge
(Mechanical operations)		Sammying	Effluents like tanning		
		(Splitting)		Unusable split	
		Shaving		Shavings	
		Trimming		Trimmings	
Post-tanning	Crust	Neutralisation			
		Retanning, Dyeing, Fatliquoring	Unexhausted process chemicals		Sludge
		Drying			
Finishing	Finished leather	Buffing, Dedusting Lacquering		Buffing dust	
		Mechanical finishing			

11. Not all the process steps from raw hide and skin to finished leather are performed in each tannery. There is some specialisation, and tanneries may work from raw hide and skin to wet blue, from raw hide and skin to crust and from wet blue or crust to finished leather.

12. Furthermore, the sequence of process steps may change depending on the raw material used, as shown in Table 3.

Table 3 Sequence of processes according to different raw hides (CEC, 1992)

Processes	Cattle	Sheep	Pig
Beamhouse	soaking	soaking	soaking
	unhairing	fleshing	unhairing
	liming	dewooling*	liming
	splitting		deliming
	deliming		deliming
	bating		bating
Tanning	pickling	pickling	pickling
		washing	
		degreasing*	degreasing*
	tanning	tanning	tanning
			splitting
	shaving		shaving
Post-tanning	retanning	retanning	retanning
	dyeing	dyeing	dyeing
	fatliquoring	fatliquoring	fatliquoring
	drying	drying	drying
Finishing	buffing		buffing
	finishing	finishing	finishing

* specific to the skin process

2.1 Curing: Hide and skin storage

13. After the hides and skins are flayed from the carcass at the abattoirs, they are delivered either to the hide and skin market or directly to the tannery.

14. Where necessary, hides and skins are cured mainly by **salting** before transport to the tannery in order to prevent them from putrefying. Salting can be done by wet salting, brining (mainly in USA), and dry salting.

15. **Chilling or cooling** the hides and skins is considered a short-term preservation method. Restrictions are that the slaughterhouse must be relatively close to the tannery and the raw material must be processed almost immediately (depending on the chilling method between one day and twenty days).

16. **Drying** is a cost-effective long-term preservation method in countries with low relative humidity and high temperatures.

17. In the tannery hides and skins can be sorted into several grades (by size, weight or quality), trimmed (some of the edges can be cut off) and stored. The cured, mainly salted hides can be stored in the tannery for several months, but cooled or chilled hides have to be processed within days. Curing is done at the abattoir or at the hide market and only in certain cases it might be necessary to repeat the step in the tannery. Skins and hides are called pelt after this procedure.

2.2 Beamhouse operations

18. The hide is prepared for tanning through several steps in the beamhouse of a tannery. The following processes are typically carried out: soaking, liming, unhairing, fleshing and splitting. The aim of these processes is wetting the cured hides and skins again to ensure the initial moisture content and removing dung, grease, and hair.

19. Typical steps are:

Soaking: Soaking is carried out to allow hides and skins to re-absorb water, which may have been lost after flaying during preservation. The process is mostly carried out in two steps: a preliminary (dirt) soak to remove the salt and dirt and a main soak. This may be carried out in pits, paddles or drums (or a combination of these). Paddle vats are semi-open systems used for skins or small hides, whereas drums (apparently the most common technique) are closed systems used for hides. The duration of soaking may range from several hours to a few days. Depending on the type of raw material additives can be used such as surfactants, enzyme preparations, and bactericides.

Liming and Unhairing: This procedure includes the removal of the epidermis layer, including hair, interfibrillary proteins and fat and opening-up the fibre structure in a bath of lime (calcium hydroxide) and sodium sulphide. Liming and unhairing can be carried out in drums, paddles, mixers or pits. The duration of this step may vary from 18 hours (drums) to 7 days (vats). Limed hides are fleshed to remove the excess tissue and muscles or fat adhering to the hide. In some cases fleshing is carried out just after soaking (green fleshing) (UNEP/IEO, 1994). By mechanical splitting often done in lime condition on splitting machines the thickness of the hides and skins is regulated.

2.3 Tanyard operations

20. Typically, the following processes are carried out in the tanyard: deliming, bating, pickling, and tanning. The tanned hides and skins are tradable intermediate products as they have now been converted to a non-putrescible material, the leather. The processes are performed in vessels such as drum, mixer or paddle.

21. **Deliming:** After liming, the lime and other alkali in the hide and skin (called pelt now) is no longer required and is removed by washing and adding controlled amounts of acids or acid-producing salts.

22. **Bating:** Bating is a partial degradation of non-collagenic protein achieved by enzymes to improve the grain of the hide and skin. It is performed to impart softness, stretch, and flexibility to the leather. This step can take between 30 minutes and 12 hours. Bating and deliming are usually performed together by placing the hides and skins in an aqueous solution of ammonium salt and proteolytic enzymes.

23. **Pickling:** Pickling is carried out to reduce the pH of the pelt prior to mineral tanning (chrome tanning) and some organic tannages (glutardialdehyde or vegetable tanning). The choice of the exact pickling parameters depends on the subsequent tanning step. Normally, the pickle float contains acids such as sulphuric acid or organic acids like formic acid and salt for avoiding the swelling of the hide. The pickling is done in drums. Fungicides used to protect intermediates against attack by fungi (mould) may be added during pickling. Very often tanning is carried out in the pickle liquor.

24. **Degreasing:** Degreasing is most relevant in processing sheepskins, but it is also required for pigskins. Excess grease must be eliminated from fatty skins to prevent the formation of insoluble chrome-soaps or fat spues in later stages. This step can be done after pickling or before liming (esp. pig skins). Solvents or surfactants can be used.

25. **Tanning:** In the tanning process the collagen fibre is stabilised by the cross-linking action of the tanning agents such that the hide (pelt) is no longer susceptible to putrefaction. Furthermore its resistance to mechanical action and heat increases.

26. The various tanning agents can be categorised in three main groups:

- Mineral tannages
- Vegetable tannages
- Alternative tannages (syntans, aldehydes, oil tannage).

27. Chromium and vegetable tanning agents are the most commonly used ones. Chrome tanning in drums takes 4 to 24 hours. Vegetable tanning is the oldest industrial tanning process in use. It is still employed for sole, saddlery, and some speciality leathers (heavy leathers). It takes one day (in drum) to 6 weeks or more (in pits) for the tanning agent (extracts) to penetrate the pelt (US-EPA, 1997; UNEP/IEO, 1994).

28. Syntans are synthetic tanning agents (e.g. made by treating aromatic substances such as phenols with formaldehyde and sulphuric acid). More recently, resins derived from polyurethans and synthetic substances derived from polyacrylic acids are used alone or in combination with other tanning agents.

29. In the group of aldehydes the glutardialdehyde is by far the most efficient cross linking agent. Studies carried out with glutardialdehyde have shown that it can be used as a tanning agent in itself to give washable leather, which is very resistant to perspiration. When it is used in conjunction with chromium salts it greatly improves the stability of the resulting leather (Bowes & Cater, 1965).

30. After the tanning process, the chrome-tanned intermediate is called **"wet blue"**, and if other tanning agents are used **"wet white"**. It can be stored and/or transported in this condition. Fungicides may be added to the tanning float for preservation of the intermediate product (UNEP/IEO, 1994).

31. Tanning is followed by draining, sammying or by shaving in order to reduce the moisture content prior to further mechanical action such as adjusting thickness (by splitting or).

2.4 Post-tanning operations

32. **Post-tanning:** Post-tanning operations involve neutralisation and washing, followed by re-tanning, dyeing and fatliquoring, mostly done in a single processing vessel. Further special operations may be carried out to add certain properties to the leather such as water repellence, oleophobing, flame retarding etc.

33. **Neutralisation:** This is the process by which the tanned hides and skins are brought to a pH suitable for the further post-tanning processes.

34. **Re-tanning:** The re-tanning process improves the feel and handle of the leather, fills the looser parts of the leather, improves the resistance to alkali and perspiration by using a wide variety of chemicals (vegetable tanning extracts, syntans, aldehydes, resins, and mineral tanning agents).

35. **Dyeing:** The dyeing process is carried out to produce a level of colour over the whole surface of each hide or skin and an exact matching between the hides and skins in a commercial pack. Typical dyestuffs are water-based acid dyes and metal complex dyes.

36. **Fatliquoring:** Leathers must be lubricated to achieve product-specific characteristics and to re-establish the fat content lost in previous procedures. The oils used in emulsions may be of animal or vegetable origin or might be synthetics based on mineral oils. Fatliquoring is usually performed in drums.

37. After this process steps the dried leather is called “**crust leather**”.

2.5 Finishing

38. The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather. Finishing operations can be divided into mechanical finishing processes and applying a surface coat. A wide range of mechanical finishing operations may be carried out like staking, buffing/dedusting, dry milling (mechanical softening), polishing, and plating/embossing. The purpose of applying a surface coat is to provide protection from e.g. water or oil, to provide colour and gloss, to provide fashion effects and to meet other customer requirements.

3. CHEMICALS

3.1 Industrial chemicals

39. The chemicals used at each process step may be grouped together according to the main processes (Table 4). Not all the process steps from raw hide to finished leather are performed in each tannery. There is some degree of specialisation and some tanneries may work from raw hide and skin to wet blue, others from raw hide and skin to crust and from wet blue or crust to finished leather.

40. During processing raw hide is reduced by weight. Therefore, a factor for **remaining mass fraction** for raw hide must be introduced, when calculating releases of chemicals that refer to the mass of hide processed in the respective process step (Hauber, 2003). For example:

- 15 t raw hide = 7.94 t wet blue sammed (1) = 5.02 t wet blue shaved (2)= 2.94 t **shoe upper leather** (3)
  This results by mean in remaining mass fractions of approximately:
  $F_{remaining\text{-}mass\ -1} = 0.5$, $F_{remaining\text{-}mass\ -2} = 0.35$, $F_{remaining\text{-}mass\ -3} = 0{,}2$;
  that means: 15 t raw hide x 0.50 = 7.50 t wet blue sammed
  15 t raw hide x 0.35 = 5.25 t wet blue shaved
  15 t raw hide x 0.20 = 3.00 t shoe upper leather,

  or
- 15 t raw hide = 5.08 t wet blue sammed (1) = 3.18 t wet blue shaved (2)= 1.48 t **upholstery leather** (3)
  This results by mean in remaining mass fractions of approximately:
  $F_{remaining\text{-}mass\text{-}1} = 0.35$, $F_{remaining\text{-}mass\text{-}2} = 0.2$, .. $F_{remaining\text{-}mass\text{-}3} = 0.1$;
  that means: 15 t raw hide x 0.35 = 5.25 t wet blue sammed
  15 t raw hide x 0.20 = 3.00 t wet blue shaved
  15 t raw hide x 0.10 = 1.50 t upholstery leather.

The remaining mass fractions $F_{remaining\text{-}mass}$ for each process step are listed in Table 4.

Table 4 Consumption of the chemicals and remaining mass fractions in main processes

Process	Stage at the end of the process	Fraction of remaining mass from raw hide $F_{remaining-mass}$	Chemicals	Consumption [kg/t] $Q_{chemical-formulation}$	Fraction of the chemical in the formulation $F_{chemical}$	Degree of fixation $F_{fixation}$
Beamhouse						
Pre-soaking	Raw hide salted	1	NaCl surfactants	150 3	1 0.7	0 0
Soaking	Raw hide	1	Na_2CO_3 surfactants Enzyme formul.*, (resp. Na_2SO_4) Bactericide	10 3 5 2	1 0.7 0.9 0.3	0 0 0 0.2
Liming	Raw hide	1	$Ca(OH)_2$ Na_2S/NaSH Auxiliary-SH Auxiliary-NH Enzyme formul.*, Sodium hydroxide	40 30 10 10 5 15	1 0.7 0.3 0.6 0.9 0.5	0 0.7 0.7 0 0.1 0
Deliming (unsplit)	Pelt	0.5 1	Acidic salts CO_2	20 30	1 1	0 0.8
Bating	Pelt	0.5	Enzyme formul.*	20	0.9	0
Tanning						
Degreasing	Pelt	0.5	Degreasing auxiliary	5	0.7	0
Pickling	Pelt	0.5	NaCl Formic acid Sulfuric acid	80 10 15	1 1 0.98	0 0 0
Tanning	Pelt	0.5	Cr tanning agent Salt Alkaline salts Fatliquor Fungicide	20 60 5 20 2	1 1 1 0.7 0.2	0.9 0 0 0.8 0.8
Post-Tanning						
Neutralisation Re-tanning Dyeing Fatliquoring Fixation (formic acid)	Shaved weight:	0.35	Alkaline salts Re-tanning agents Dyestuffs Fatliquor Fixation auxiliary Cationic polymer	20 150 80 150 20 15	1 0.5 0.6 0.6 1 0.2	0 0.8 0.8 0.7 0 0.9
Finishing						
Finishing	Crust weight	0.2	Washings + spraying losses	15	0.1	0

(*) Enzyme concentration ≤ 0,1%; active ingredient not detectable in effluent treatment plant

3.2 Biocides

41. There are several stages for an attack of microorganisms before hides or skins are turned into leather. Because of transport and a long-term storage it is necessary to preserve the extremely sensitive hides and skins to avoid losses through deterioration caused by bacteria.

42. In recent years the specialization between tanneries resulted in a considerable movement of hides and skins in the semi-processed state. The most common form of partially produced leather is in the wet blue (chrome tanned) or wet white (chrome-free, mainly aldehyde tanned) and the crust (dry, perhaps dyed) condition. Semi-processed leathers like wet blue and wet white are due to their water content and acidity extremely sensitive to attack by mould and yeast but not by bacteria.

43. Biocides can be applied in tannery processes to protect the substrate against either bacterial (bactericides) or fungal (fungicides) attack. Bactericides are not normally used in curing the hides but in the tannery for preservation of soaking. One of the most frequently used active agents is didecyldimethylammonium chloride, a quaternary ammonium salt that effects rapidly, has a low toxicity, and is biodegradable.

Other microbicides used for soak preservation are:

- sodium dimethyldithiocarbamate,
- N-hydroxymethyl-N-methyldithiocarbamate,
- tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione and
- 2-thiocyanomethylthiobenzothiazole (TCMTB) that is rather a fungicide.

Addition rates range between 0.02-0.1% formulation calculated on rawhide weight.

44. To protect partially processed hides against mould growth fungicides are used suited to guarantee long-term preservation (several months) after application by preference in the tanning liquor. One third to one half of the addition rate can also be given to the pickle float.

45. Several years ago the predominant fungicides used in the leather industry were based mainly on chlorinated phenols. Since the withdrawal of pentachlorphenol (PCP) alternative products are offered. However, there are other phenol derivates, such as p-chloro-m-cresol (PCMC), and ortho-phenylphenol (OPP). Both fungicides are also used in vegetable tannage and mainly combined with each other. Alternatives to PCP presenting low toxicity and ecotoxicity fungicides data are also found among heterocyclic nitrogen and sulphur compounds, but they are less effective than PCP.

46. The most important and best known fungicides for use in the leather industry are (Lindner, 1998):

- 2-thiocyanatomethylthiobenzothiazole (TCMTB)
- 2-n-octyl-4-isothiazolin-3-one (OIT)
- 4-chloro-3-methylphenol (PCMC)
- ortho-phenylphenol (OPP)
- 2-benzimidazolyl-methylcarbamate (BCM)
- 1,2-benzisothiazolin-3-one (BIT).

47. In some cases the combination of several fungicides is recommended to extend the effect against fungal species. The application rate of the formulation is 0.01 – 0.5% calculated on the pelt mass after splitting.

48. Biocides are applied with water directly in drums or mixers during soaking, pickling or tanning. Generally biocides may be included in liquid chemical formulations such as dyestuffs, fatliquors or casein finishes (BREF, 2003). Furthermore, raw hides and skins may contain biocides applied to the animal to protect it from decease during its life.

4. RELEASE ESTIMATION

49. The emissions of the tanning industry may be in gaseous, liquid and solid form. They arise from the consumption of raw hides, energy, chemicals, and water. The main releases to wastewater originate from wet processing in the beamhouse, the tanyard and the post tanning operations. The main releases to air are due to the dry-finishing processes, although gaseous emissions may also arise in all other parts of the tannery. The main sources of solid wastes originate from fleshing, splitting, and shaving. A further potential source of solid waste is the sludge from the sewage treatment plant in case this is operated by the tannery on site.

4.1 Releases from cured hides

50. The usual technique employed for preventing raw hides from deterioration during storage and/or transportation is salting. In general, there are no biocides used in the preservation of bovine hides in Europe. However hides and skins can contain traces of biocides because animals were treated with these substances.

51. **Wastewater emissions**: Process-specific substances, such as salt or traces of biocides used during the life of the animal can be found in the joint effluents after subsequent process steps are performed.

4.2 Releases during beamhouse operations

52. **Wastewater emissions:** The soak liquor is discharged to the wastewater treatment plant. If the hides or skins were preserved the effluents contain most of the salt. The additives employed in soaking, e.g. bactericides are largely contained in the soak liquor. The effluents of liming and unhairing are characterised by their high alkalinity and their high sulphide content.

53. **Air emissions:** Sulphides might be released to air from any effluents carrying sulphides, if the pH drops below 9. If the sulphide solution is alkaline (pH above 8.5-9) hydrogen sulphide is not released.

4.3 Releases during tanyard operations

54. **Wastewater emissions:** Effluents from pickling are acidic and high in salt concentration. Many tanneries carry out the tanning process in the same float. Emissions such as unused tanning agents and traces of fungicides will therefore be contained in the tanning float.

55. **Air emission:** Sulphides carried over with the hides from liming can give rise to some free hydrogen sulphide in the subsequent processes.

4.4 Releases during post-tanning operations

56. **Wastewater emissions:** Emissions from the post-tanning operations deriving from neutralising agents, retanning agents such as vegetable tannins, syntans, polymers, and mineral tanning agents, fatliquors, and dyestuffs occur mainly to wastewater. Due to the cost of dyestuffs dyeing is one of the most expensive processes carried out in a tannery; bath exhaustion is therefore required to be maximised.

4.5 Releases during finishing operations

57. **Air emission:** Different emissions arise depending on the type of chemicals and process used. If organic solvents are used, there are several potential sources of air emissions in the finishing of leather. Yet, non-solvent (water-based) finishing technologies are now developed and associated releases are much lower. Equipment for wet scrubbing the exhaust air has become a standard installation in spraying units. Cleaning procedures are indispensable to limit air emissions.

4.6 Releases during other life cycle stages

58. Releases may occur during other life-cycle stages, e.g. the final use of leather articles and the disposal of leather articles.

59. A large part of the biocides remaining in the finished articles can be released to the environment during the service life of the leather articles. For volatile substances, a release to the atmosphere can be assumed. Furthermore for articles subject to cleaning, substantial releases to wastewater can be assumed.

60. All of these releases will be diffuse and relevant only for a regional exposure assessment. No precise quantitative release estimations can be proposed for the time being.

4.7 Water consumption

61. A distinction has to be made between the rates of water consumption of plants processing raw hides to finished leather and plants specialised in processing from wet-blue to finished leather. In the first case, water consumption rates are commonly in the range of 25-80 $m^3.t^{-1}$ of raw hide (UNEP/IEO, 1994) with a median value of 35 $m^3.t^{-1}$ (EU, 1996) or in Germany of 21 $m^3.t^{-1}$ of finished leather (Böhm et al., 1997, 2000; Hillenbrand et al. 1999). Table 5 provides detailed figures on averaged water consumption.

Table 5 Averaged water consumption in various process units for bovine salted hides and chrome tanning (BREF 2003)

Stage	Process	Water Consumption $m^3.t^{-1}$ raw hide
Beamhouse	soaking	2-3
	liming and unhairing	3-7
	Subtotal	**5-10**
Tanning	deliming and bating	4-9
	pickling and chrome tanning	0.5-3
	washing	
	Subtotal	**4.5-12**
Sammying		0.2
Post-tanning	washing, neutralisation	5-7
	washing after neutralisation	1-3
	retanning, dyeing fatliquoring	2-6
	washing dressing, cleaning	2-5
	Subtotal	**10.2-21.2**
Finishing		
Total volume of wastewater		***19.7-43.2***

4.8 Wastewater treatment

62. The main source of release to wastewater in tanneries is unused active substances in spent baths. Cleaning containers or machinery washings contribute to a very little extent to these emissions.

63. Tanneries generate effluents that are typically high in organic and inorganic pollutants. Their effluents are complex in nature and with variation in characteristics from time to time, process-to-process, and tannery-to-tannery, since tanneries employ a sequence of batch processes and a wide range of raw materials. Tannery effluents have to be treated before they can be discharged to surface water. Depending on local economic conditions and their geographic location, tanneries may treat wastewater on-site, discharge directly to the municipal sewer or use a combination of these options. Furthermore, some tanneries can discharge their treated effluent directly to surface waters.

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 wastewater effluents. Chromium (III) is mainly coming from the tanning process. For this reason on-site pre-treatment of wastewater is common practice. This leads also to a partial removal of substances (e.g. dyes) from the aqueous phase by co-precipitation.

65. The wastewater treatment strategies employed by tanneries are so varied that it is difficult to generalise, but the classical scheme is:

- mechanical pre-treatment: skimming of fats, oil, and grease, sedimentation

- physico-chemical treatment: includes equalising flows, neutralisation, oxidation of sulphide from the beamhouse, precipitation of chrome from tanning and post-tanning processes, sedimentation or flotation. It is mainly performed to remove organic matter, sulphide and chrome.

- biological treatment: reduction of the high organic content. It may include nitrification/denitrification steps gradually introduced in countries with strict nitrogen discharge limits.

- sedimentation: separation of activated sludge from the purified overflow.

- Sewage sludge: This surplus sludge is collected and treated together with the primary sludge from mixing and equalising. To reduce the sludge volume a dewatering step is often practised.

66. In most countries, tanneries have to carry out a pre-treatment of their wastewater for sulphide and chrome. Strict discharge limits must be met before effluents to a municipal water treatment plant where the biological treatment is done are discharged. Tanneries discharging directly to surface water have to meet additionally the requirements for COD, BOD (chemical and biological oxygen demand) and nitrogen so they have to treat the wastewater biologically, too. A recent German study revealed the following data. Out of a total of 30 German tanneries 5 plants (17%) discharge their wastewater after pre-treatment and biological treatment directly into surface waters and 25 plants after mechanical and physico-chemical treatment into municipal sewage treatment plants (Böhm et al, 1997, 2000; Hillenbrand, 1999).

4.9 Solid waste from hide processing to leather

67. Only 20-25% of the raw hide weight is processed to leather (see Table 4 and Figure 1). Residues include salt, hair (or wool) trimmings, fleshings, splits, shavings, fat, grease, waste machinery oil, sludge from wastewater treatment, waste treatment, waste process chemicals from finishing operations and others (UNIDO, 2000). Residues from tanneries can be tradable products, raw material for other branches (e.g. fleshings, lime split, shavings, grease) depending on markets and facilities. Currently many residues are being disposed of, generally in landfills.

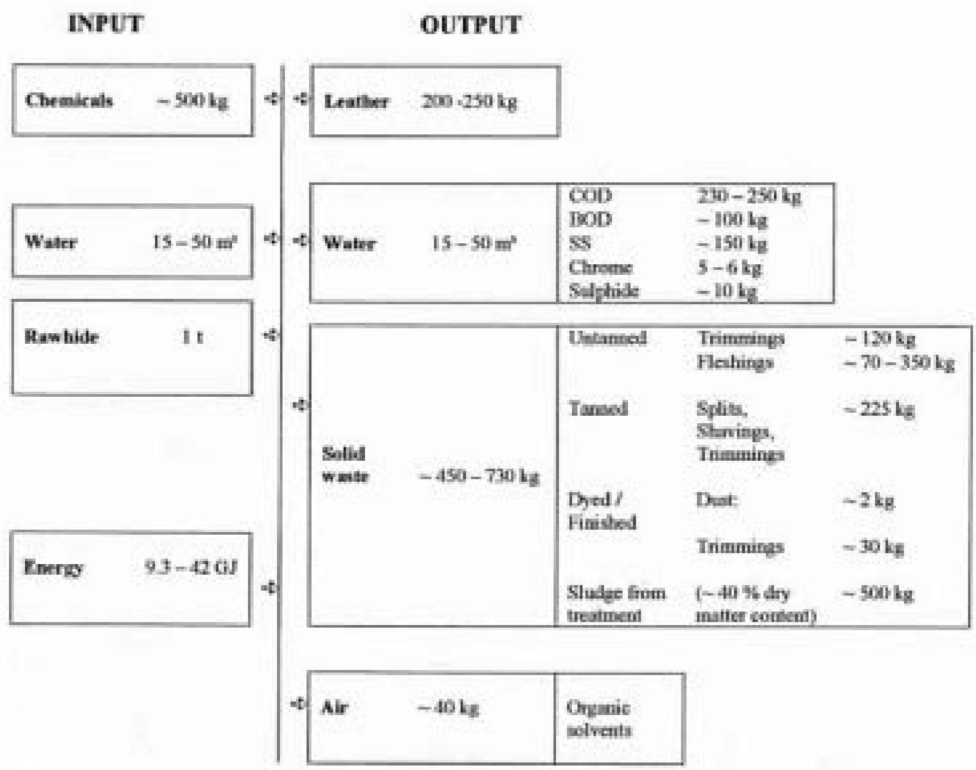

Figure 1 Input* and output overview for chrome-tanning of 1 tonne salted bovine hides (BREF 2003, p. 5); * = 500 kg chemicals input include approx. 200 kg curing salt

4.10 Solid waste from used leather products

68. 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.

5. BRANCH SPECIFIC PARAMETERS

5.1 Daily production volume ($Q_{rawhide}$) of a representative point source

69. New statistical data for wastewater quantities, dilution factors and production quantities for the leather processing industry were obtained and statistically evaluated in a recent research project "Abwassereinleiter-Statistik" (wastewater statistics) of Umweltbundesamt (Böhm et al. 1997, 2000). A comprehensive questionnaire was sent to companies in this branch and the data received were used to examine standard default values applied in the EU for risk assessment in the aquatic compartment, e.g. the production volume per day ($Q_{rawhide}$), the flow rate of sewage treatment plant ($EFFLUENT_{stp}$) and the dilution factors of receiving water (DILUTION). The return rate of the questionnaire was 78%, so that the survey can be considered as representative for Germany and the data could be evaluated statistically.

70. The statistics of this study, based on the EU standard values EFFLUENTstp = 2000 $m^3.d^{-1}$ and DILUTION factor of 0.1, provide a realistic worst case for the daily production volume of a generic German leather processing plant: $Q_{rawhide}$ = **15 $t.d^{-1}$ raw hides**. This default value should be taken as realistic worst case for the local emission calculation, when no detailed – in the best case statistically based – data for the daily production volume are known.

71. The weight of raw hides and skins is reduced in each processing step. This reduction is taken care by the remaining mass fraction: $F_{remaining-mass}$ (see chapter 3.1). This is important for the amount of chemicals or biocides that are used in the each processing step because this amount is normally based upon the actual weight of the hide or skin (or pelt) in the respective processing step (beamhouse, tanning, posttanning and finishing (see Table 4).

5.2 Number of working days

72. The median of number of working days in 1995 was 220; arithmetical mean: 227 days per year. (Böhm et al. 1997, 2000).

5.3 Leather dyeing

73. The dominant source of dyestuff released from tanneries is the draining of used dye bath solutions. Acid dyes (which account for about 90 % of the market), metal complex dyes, and scarcely used, cationic dyes are applied as leather colorants. Two types of dyeing methods are in use:

- drum dyeing (dominant) and
- brush staining.

74. Using general estimates for parameters such as type of dyeing, liquor ratio and equilibrium constant some degrees of fixation ($F_{fixation}$), are given in Table 4 as example. The fixation rate depends not only on the compound used, but also on the conditions of use.

75. Table 6 shows that 9% of the plants dye the total daily production with one dyestuff. On the average 73% of the plants dye less than half of the daily production with one dyestuff (>20 - 50%). The fraction of the daily production ($F_{daily-production}$) that is dyed with one dyestuff per day is set to **50%.**

Table 6 Fraction of the daily production dyed with one dyestuff (Böhm et al., 1997, 2000)

Fraction of main dye per day [%]	**Plants [%]**
0	**5**
>0 - 20	**41**
>20 - 50	**27**
>50 - 99	**18**
100	**9**

6. EMISSION SCENARIOS

76. The emissions of the life cycle stages “production” and “formulation” of the chemicals used in leather processing can be calculated by applying the appropriate A- and B-Tables of the Technical Guidance Document [EU, 2003]. This document presents the algorithm for calculation the emissions of the "industrial use" life cycle stage to the local water compartment. If relevant, the “soil” and the “air” emissions can be calculated with the respective A- and B-Tables of the Technical Guidance Document (EU, 2003). Emissions from leather articles during the "service life" cycle stage and the "disposal" of leather products are not covered.

77. The scenarios in this report have the following structure:

Variable/parameter	Symbol	Unit	Default	S/D/O	Remark

The parameters of the calculation are the input and the output of the scenario. The S, D, O classification of a parameter indicates the status:

S Parameter must be present in the input data set. This value is presented by the applicant or, if not, the value is taken from a “pick list” (e.g. Table 4).

D Parameter has a default value. It can be changed by the assessor for site-specific calculations.

O Parameter is the output from the calculation.

78. The emission estimation presented in this document is performed on a local scale. The predominant pathway is from the plant discharges via the facility and municipal sewage treatment plant to receiving surface waters.

79. Biocides can be applied in each of the following steps: soaking, pickling and tanning. It can be assumed, in a “worst case” situation, that one and the same biocide is applied in each of those steps. Fungicides are added to the pickling or the tanning process or one part is added to the pickle, the rest to the tanning float.

6.1 Emission calculation for industrial chemicals and biocides

Leather processing: pathway to wastewater

Table 7 Emission scenario for chemicals used in leather processing

Variable/parameter	Symbol	Unit	Default	S/D/O	Remark
Input:					
Mass of processed raw hide per day	$Q_{rawhide}$	$t.d^{-1}$	15	D	Section 5.1
Factor of remaining mass of rawhide at specific step "x"	$F_{remaining\text{-}mass}$	-		D	Table 4
Mass of chemical formulation used per mass at specific step "x"	$Q_{chemical\text{-}formulation}$	$kg.t^{-1}$		D/S	Specific or Table 4
Content of chemical in formulation	$F_{chemical}$	-		D/S	Specific or Table 4
Degree of fixation - Proportion of the substance chemically converted or fixed to the hide during processing	$F_{fixation}$	-		D/S	Specific or Table 4
Fraction of the daily production that is treated with the specific chemical[1]	$F_{daily\text{-}production}$	-	0.50	D	Section 5.3
Fraction of chemical eliminated by on-site waste water treatment before discharge to a municipal sewage treatment plant[2]	$F_{on\text{-}site\text{-}treatment}$	-	0	D/S	Section 4.8
Output:					
Local emission of chemical to waste water per day for a specific process step "x"	$Elocal_{x\text{-}water}$	$kg.d^{-1}$	-	O	

Model calculation:

$$Elocal_{x\text{-water}} = Q_{rawhide} \times F_{remaining-mass} \times Q_{chemical-formulation} \times F_{chemical} \times (1 - F_{fixation}) \times F_{daily-production} \times (1 - F_{on-site-treatment}) \quad (1)$$

Remark:
If one and the same chemical e. g. active ingredient in biocides is applied in several process steps, the results of each $Elocal_{x\text{-water}}$ must be summed.

[1] This value should be used only for dyes. For other chemicals than dyes this fraction should be taken as default value of 1.

[2] In generic calculations this fraction is set default = 0. Leather manufacturers may apply on-site knowledge and introduce a site-specific fraction for elimination of chemical on-site sewage treatment.

$$Elocal_{total\text{-}water} = \sum Elocal_{x\text{-}water} \tag{2}$$

6.2 Service life of leather products

No quantitative release estimations can be proposed for the time being (see also chapter 5.6).

6.3 Disposal of leather products

The disposal of leather products is not quantified yet.

7. EXAMPLES OF CALCULATION

For a dye in the dyeing process the following emission is calculated:

Input:

$Q_{rawhide}$ = $15\ t.d^{-1}$
$F_{remaining\text{-}mass}$ = 0.35
$Q_{chemical\text{-}formulation}$ = $80\ kg.t^{-1}$
$F_{chemical}$ = 0.60
$F_{fixation}$ = 0.80
$F_{daily\text{-}production}$ = 0.50
$F_{on\text{-}site\text{-}treatment}$ = 0

Output:

$Elocal_{dyeing\text{-}water}$ = $15\ t.d^{-1} \times 0.35 \times 80\ kg.t^{-1} \times 0.6 \times (1\text{-}0.8) \times 0.5 \times (1\text{-}0) = 25.2\ kg.d^{-1}$
$Elocal_{total\text{-}water}$ = $Elocal_{dyeing\text{-}water}$ (chemical is used only for the dyeing process)

For a chrome tanning agent in the tanning process the following emission is calculated:

Input:

$Q_{rawhide}$ = $15\ t.d^{-1}$
$F_{remaining\text{-}mass}$ = 0.5
$Q_{chemical\text{-}formulation}$ = $20\ kg.t^{-1}$
$F_{chemical}$ = 1.0
$F_{fixation}$ = 0.9
$F_{daily\text{-}production}$ = 1.0
$F_{on\text{-}site\text{-}treatment}$ = 0

Output:

$Elocal_{tanning\text{-}water}$ = $15\ t.d^{-1} \times 0.5 \times 20\ kg.t^{-1} \times 1.0 \times (1\text{-}0.9) \times 1.0 \times (1\text{-}0) = 15.0\ kg.d^{-1}$
$Elocal_{total\text{-}water}$ = $Elocal_{tanning\text{-}water}$ (chemical is used only for the tanning process)

For an bactericide in the soaking process the following emission is calculated:

Input:

$Q_{rawhide}$ = $15\ t.d^{-1}$
$F_{remaining\text{-}mass}$ = 1.0
$Q_{chemical\text{-}formulation}$ = $2\ kg.t^{-1}$
$F_{chemical}$ = 0.3
$F_{fixation}$ = 0.2
$F_{daily\text{-}production}$ = 1.0
$F_{on\text{-}site\text{-}treatment}$ = 0

Output:

$Elocal_{soaking\text{-}water}$ = $15\ t.d^{-1} \times 1.0 \times 2\ kg.t^{-1} \times 0.3 \times (1\text{-}0.2) \times 1.0 \times (1\text{-}0) = 7.2\ kg.d^{-1}$

For an fungicide in the tanning (or pickling) process the following emission is calculated:

Input:

$Q_{rawhide}$ = 15 $t.d^{-1}$

$F_{remaining\text{-}mass}$ = 0.5

$Q_{chemical\text{-}formulation}$ = 2 $kg.t^{-1}$

$F_{chemical}$ = 0.2

$F_{fixation}$ = 0.8

$F_{daily\text{-}production}$ = 1.0

$F_{on\text{-}site\text{-}treatment}$ = 0

Output:

$Elocal_{tanning\text{-}water}$ = $15\ t.d^{-1} \times 0.5 \times 2\ kg.t^{-1} \times 0.2 \times (1\text{-}0.8) \times 1.0 \times (1\text{-}0) = 0.6\ kg.d^{-1}$

If one and the same active ingredient is applied as bactericide and as fungicide, the results of each $Elocal_{x\text{-}water}$ must be summed.

$$Elocal_{total\text{-}water} = Elocal_{soaking\text{-}water} + Elocal_{tanning\text{-}water}$$

$$Elocal_{total\text{-}water} = 7.2\ kg.d^{-1} + 0.6\ kg.d^{-1} = 7.8\ kg.d^{-1}$$

8. GLOSSARY

Bating**:** Is the manufacturing step which follows liming and precedes pickling. The purpose of bating is to delime the hides, reduce swelling, peptise fibres, and remove protein degradation products.

Beamhouse: Is that portion of the tannery where the hides are washed, limed, fleshed and unaired, when necessary, prior to the tanning process.

Buffing: Process of removing the grain layer of leather from a cattle hide mechanically with an appropriate abrasive paper. Giving the leather a nap or suede effect.

Crust leather: Leather, which has simply been dried after tanning, retanning and dyeing without a further finishing step.

Deliming: Removing the lime from hides coming from the beamhouse before tanning, by the action of inorganic or organic acids or salts of these acids.

Embossed leather: Leather embossed or printed with a raised pattern either imitating or resembling the grain pattern of some animal, or quite unrelated to a natural grain pattern.

Fleshing: Removing sub-cutaneous tissue, fat and flesh adhering to the hide, by the mechanical action of a cylinder equipped with cutting blades.

Finishing: a) Mechanical finishing operations to improve the appearance and the feel of the leather e.g. conditioning, staking, buffing, dry milling, polishing, plating/embossing.
b) Applying a pigmented or a fixing surface coat to the leather.

Hides: Are raw skins of mature or fully-grown animals of the larger kind, e.g. cattle.

Leather: Is a general term for hide or skin which still retains its original fibrous structure more or less intact, and which has been treated so as to be non-putrescible.

Lime Split: Leather that has been split into two ore more layers in the pre-tanned state (limed state).

Pelt: Refers to the hide and skin from which the hair or wool, epidermis and flesh have been removed in preparation for tanning.

Pickling: The process that follows bating to further reduce the pH prior to tanning by using salt and acid. Small hides may be stored and transported in this condition.

Retanning: Subjecting a skin or hide, which has been first more or less completely tanned by one process or one kind or blend of tanning materials, to a second tanning process involving similar or, more usually, different tanning materials.

Sammying: Removing excess moisture from the wet blue.

Skins: Are raw skins of mature, fully-grown animals of the smaller kinds, e.g. sheep, reptiles, or of the immature animals of larger species, e.g. calf.

Tanning: Processing whereby putrescrible raw hides and skins are converted into leather.

Wet blue: A hide or skin, which has been subjected to the usual beamhouse processes, has been chrome-tanned, therefore turned blue, and left wet. It may be stored or transported in this state.

Wet white: A hide or skin, which has been subjected to the usual beamhouse processes, has been tanned with chemicals other than chrome, turned white, and left wet. It may be stored or transported in this state.

Please see also:
http://www.dctleathers.com/glossary_dg.html http://www.aplf.com/en/glossary.asp?key_char=A

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