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Supplement to the methodology for risk evaluation of biocides
Emission scenario document for biocides used as preservatives in the leather industry
(product type 9)

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1. INTRODUCTION.

The purpose of this document is to provide realistic scenarios for the environmental releases of biocides used in the leather industry.

"Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Leather is produced from skins of four different types of wild and domestic animals: cattle, sheep (and lamb), goat and "reptiles & others". 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 fibriform structures. These structures are stabilised internally and laterally (cross linked) by H-bonds between the peptide groups of amino acids (EU, 1996).

Tanning is the process by which animal hides (skin of large animals such as cattle) and skins (small animals such as sheep, goat, etc.) are converted into leather. In this process, the H-bonds are replaced by substances like chromium sulphate, alum or vegetable tanning agents to stabilize the material against microbial proteolytic enzymes in wet environment, prevention of fracturing in dry environment and of gluing in hot surrounding (UBA, 1998).
Biocides are applied to prevent hides and skins from deterioration during transport, storage and treatment processes.

There are about 3 200 tanneries in Europe (Reymondon et Aloy, 1999). The most important producer and transformer in Europe is Italy (77% of all companies), followed by Spain. Size distribution of tanneries in Europe and France is shown below (table 1).

Table 1: Size of tanneries in Europe and France (Cotance, 1999; Syndicat de la Tannerie Française, personal communication, 1999) based on the number of employees.

States	**Number of tanneries**	**Size of tanneries (%)**		
		Small (< 50*)	**Medium (50-250*)**	**Large (> 250*)**
Europe	3 132	59	35.5	5.5
France	96	87.5	12.5 **	0

* number of employees.
** only one company with more than 200 employees.

The scenarios in this report are presented in the following way:

Input

[Variable/parameter (unit)] [Symbol] [Unit] S/D/O/P

These parameters are the input to the scenario. The S, D, O or P classification of a parameter indicates the status:

S Parameter must be present in the input data set for the calculation to be executed (there has been no method implemented in the system to estimate this parameter; no default value is set).

D Parameter has a standard value (most defaults can be changed by the user)

O Parameter is the output from another calculation (most output parameters can be overwritten by the user with alternative data).

P Parameter value can be chosen from a "pick-list" of values.

c Default or output parameter is closed and cannot be changed by the user.

Output

[Symbol] [Description]

Intermediate calculations

Parameter description (Unit)

[Parameter = equation] (Equation no.)

End calculations

[Parameter = equation] (Equation no.)

2. MAIN PROCESSES

The four steps of processing hides and skins are (figure 1):

- Curing
- Beamhouse operations which wash and soak the hides or skins and (at most tanneries) remove the attached hair.
- Tanyard processes in which the tanning agent (primarily chromium) reacts with and stabilizes the proteinaceous matter in the hides or skins.
- Finishing or post-tanning processes.

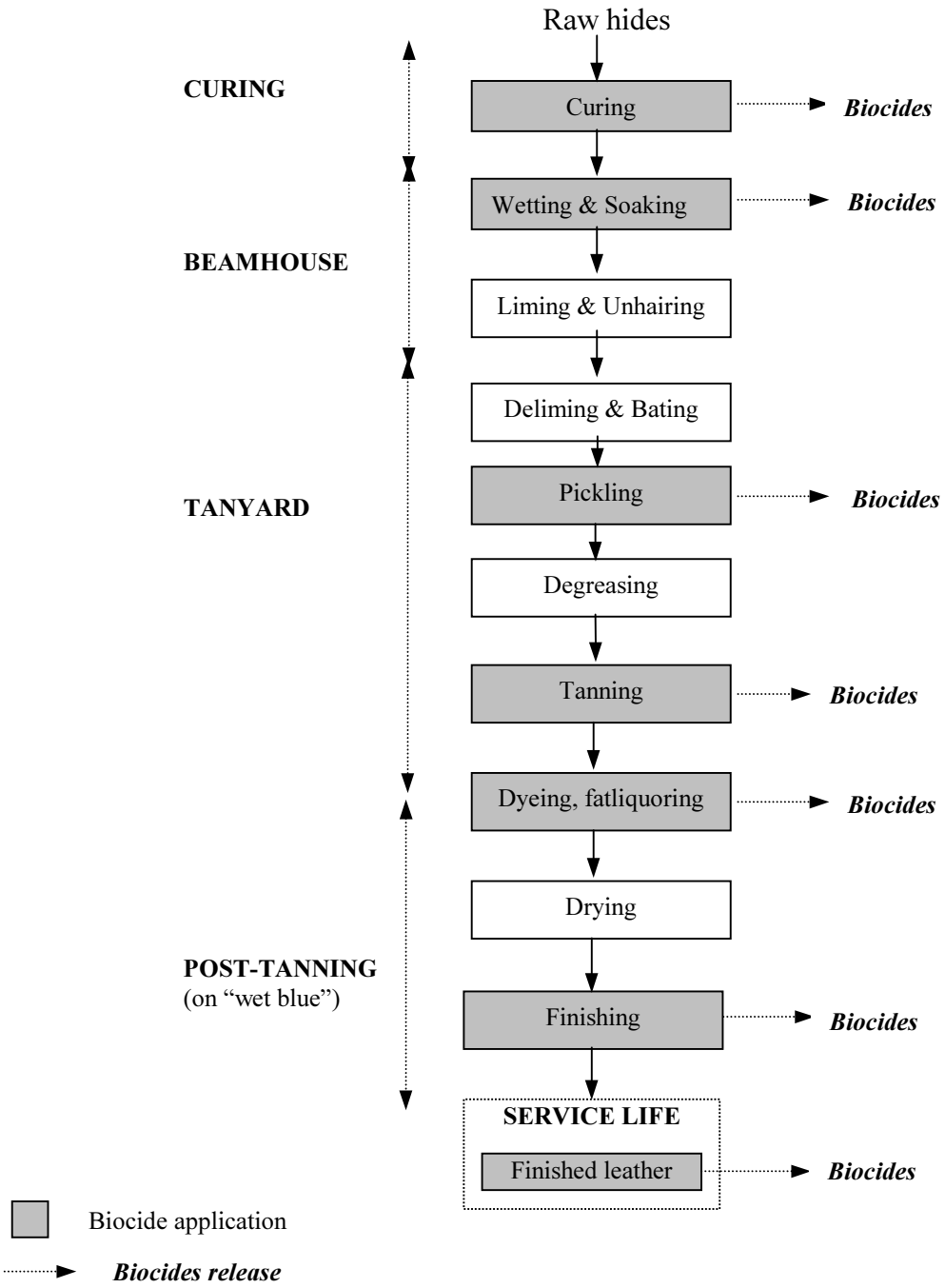

Figure 1: Main processes and releases of the "leather tanning".

Not all process steps are performed in every tannery and their sequence may change depending on the hides, as shown in table 2.

Table 2: Sequence of processes according to different hides (CEC, 1992).

HIDES	Cowhides	Sheepskin	Pigskin
PROCESS	soaking	soaking	soaking
	unhairing	fleshing	unhairing
	liming	dewooling*	liming
	deliming		deliming
	bating		bating
	pickling	pickling	pickling
		washing	
		degreasing*	degreasing*
	tanning	tanning	tanning
	splitting		splitting
	shaving		shaving
	retanning	retanning	retanning
	dyeing	dyeing	dyeing
	fatliquoring	fatliquoring	fatliquoring
	drying	drying	drying
	buffing		buffing
	finishing	finishing	finishing
	plating	ironing	plating

* specific to the skin process.

2.1. Curing.

Curing prevents deterioration of the fresh skin or hide during storage and transport. It can be performed according to three methods:

Drying: which is used mainly in warm countries where salt is not available. Dry skins can be kept indefinitely.

Salting: the addition of salts helps the skin to dry more quickly and wet back more easily. Salting can be wet salting (less practical), brining (USA) or dry salting.

Chilling: it represents only 2% of the treated hides and consists of applying cool air or ice [2 – 6°C] for a maximum storage of 3 weeks.

Usually, the skin is preserved by salting. Although salt is an excellent preservative, halophilic or halotolerant bacteria may grow on the cured hides causing "red or purple heat" (chromogenic pink, red or violet coloured bacteria). Chemicals are added to the salt to prevent red heat, such as sodium metabisulphite, boric acid and naphtalene (at 1 – 2% of the salt weight). Furthermore biocides are tested as an alternative for salt. The skin can be immersed in a biocide, or the biocide can be sprayed on the flesh surface of the hide (Bioexpo, 1998).
The salted hides and skins are stored on pallets in ambient and fresh conditions. Curing often incorporates treatment with insecticides (e.g. pyrethrum, permethrin, p-dichloro-benzene, etc.) to discourage attacks of beetles or other insects during storage and transport.

2.2. Beamhouse.

The hide is prepared for tanning through several steps of cleaning (removing the grease and hairs) and by ensuring the correct moisture content.

Typical steps are:

Wetting and soaking: the initial water content of the untanned leather is adjusted, mainly by two-stage cleaning of the skin, preliminary and main soaking. This may be carried out in pits, paddles or drums (or a combination of these). Paddle vats are semi-open systems used for small skins or dried hides, whereas drums (apparently the most common technique) are closed systems used for bovine hides. Drums can contain up to 10 tonnes of hides.

Liming and Unhairing: removal of the upper epidermis layers, including hairs etc. in a bath of lime (calcium hydroxide) and sodium sulphide. The duration of this step may vary from 18 hours (drums) to 7 days (vats). Limed hides are fleshed to remove the excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. In some cases, fleshing is carried out just after soaking (green fleshing)(UBA, 1998; UNEP/IEO, 1994).

2.3. Tanyard operations.

Deliming: the hides are washed and undergo a neutralising treatment to remove the lime. This removal is necessary to make the skins receptive to the subsequent tanning.

Bating: it is an enzymatic process 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 in an aqueous solution of ammonium salt and proteolytic enzymes at 27°C to 32°C.

Pickling: a solution containing acids (HCl, H_2SO_4, organic acids, NaCl) and salts is incorporated to adjust the pH according to the tanning requirement (stabilises the skins, end the bating action and improve the penetration of the subsequent tanning step). This step is done in drums. Fungicides such as thiobenzothiazol may be added during pickling.

Degreasing: this step, always after pickling, is required for sheep and pigskins where wool or hair may be recovered. For pigskins, degreasing can be initiated before liming. Solvents or surfactants can be used (surfactants especially if there is no recovery).

Tanning: it is the stabilisation of the collagen structure of the hide, using natural or synthetic chemicals. There are different techniques of tanning: chrome tanning, vegetable tanning, syntans and alternative tanning materials (e.g. oil tanning, limited to "chamois").
In most cases, chromium (III) salts, and sometimes additionally aluminium and zirconium salts, are used as tanning agents. Leather for clothing, shoes and industrial purposes, is chrome tanned in drums for 4 to 24 hours.
Vegetable tanning is the oldest process in use in the leather tanning industry. It is still employed for sole, saddlery and some speciality leathers (heavy leathers). It takes one day (in drum) to 6 weeks (in pits) for the tanning material (bark or wood) to penetrate the hide (UBA, 1998; US-EPA, 1997; UNEP/IEO, 1994).

Syntans are synthetic tanning agents (e.g. sulphonated products of phenol, cresol and naphtalene, or resins derived from polyurethanes or polyacrylic acids) only used for certain speciality leathers, or in association with other tanning agents.
Of the aldehydes, glutaraldehyde is by far the most efficient crosslinking agent. Trials carried out with glutaraldehyde have shown that it can be used as a tanning material in itself to give a washable leather which is very resistant to perspiration and when used in conjunction with chromium salts greatly improves the stability of the resulting leather (Bowes & Cater, 1965).
After the tanning process, the leather is called "wet blue" (for chrome tanning) or "wet white" (if other tanning agents are used). It can be stored and/or transported in this condition. Some fungicides may, then, be added for preservation (UNEP/IEO, 1994).

2.4. Post-tanning or finishing operations.

After sammying the hides to remove excess moisture, splitting or shaving (to adjust the leather thickness to the required characteristics) and trimming, post-tanning operations such as dyeing, fatliquoring or finishing can proceed.

Dyeing and fatliquoring: fatliquoring is the process of introducing oil (in an emulsion form) into the skin before the leather is dried to replace oils lost in beamhouse and tanyard processes. Fatliquoring is usually performed in a drum using an oil emulsion at temperatures of about 60°C to 66°C for 30 to 40 minutes.

Finishing: The finishing process refers to all the steps that are carried out after drying. Leather may be finished in a variety of ways: buffed with fine abrasives to produce a suede finish; waxed, shellacked, or treated with pigments, dyes, and resins to achieve a smooth, polished surface and the desired colour; or lacquered with urethane for a glossy patent leather. Having been tanned, the finished leather is relatively safe from destruction by micro-organisms. However, as it contains oils and greases added to the leather in the finishing steps, it is susceptible to moulds. Mildew is undesired from an aesthetic point of view, and can cause stiffness and cracking of the leather due to removal of oils and greases used in the finishing operations (Bioexpo, 1998). Biocides can be applied by padding, spraying or rolling (UNEP/IEO, 1994).

Remark
Leather that has been processed through soaking, liming, deliming, pickling and tanning, and that is stored for some time or sold to another tannery, is designated as "wet-blue leather".
"Crust leather" is the leather before the finishing step.

3. BIOCIDES.

The application of biocides is independent of the type of hides or tanning (table 3). The main application is during storage before tanning or finishing steps. Thus, small tanneries, which process hides and skins without intermediate storage don’t need to use biocides or in very limited quantities. Thin hides, more sensitive to biological deterioration, seem to need more biocide than thicker material.
Several biocides, usually two, may be used alternatively in the same year to avoid the phenomenon of resistance. Best practice is to change the active ingredients in the bactericide and fungicide on a regular basis; say, every six months (IPPC, 2000).

Table 3: Performance chemicals, in kg/100 kg hides (UNEP/IEO, 1994).

Performance Chemicals	Heavy Leather*	Light Leather*
Bates	0.8	0.8
Biocides	**0.1 – 0.4 ****	**0.02 – 0.2 ****
Syntans		3
fat liquor		4
dyeing auxiliaries		3.8
Dyes		0.6
Finishes		4

* The distinction between heavy and light leather is related to the animal size. Representative hide weights are (UNEP/IEO, 1994):

– bovine (heavy) 15-40 kg / animal
– sheep (light) 1-3 kg / animal
– pigskin (light) 2-4 kg / animal

** based on a 30% active substance content (personal communication Rhodia, 2000)

Biocides can be applied in various tannery processes to protect the substrate against either bacterial (bactericide) or fungal (fungicide) attack. Preservatives are used at many different stages in the leather industry. Biocides may be added in each of the following steps: curing (salting), soaking, pickling, tanning, dyeing and finishing. The steps immediately prior to storage or transport are the most critical. This would include curing, tanning and finishing. There are no data available concerning the semi-open systems; concerning closed systems, biocides are incorporated with water directly in drums during soaking, pickling, tanning, dyeing and wet-finishing. Generally biocides are included in most liquid chemical formulations such as dyes, fatliquors and casein finishes (IPPC, 2000).
The application rates of biocides vary widely from tannery to tannery. Some examples of application rates are given in table 4. Nowadays, the general trend is to reduce the use of biocides.

Table 4: Quantities of common biocides (Centre Technique du Cuir (CTC) personal communication, 1999).

Step	Amount of substance applied per mass of raw hides (%)
Curing (salting)	0.01 – 0.5
Soaking	0.01 – 0.5
Pickling	0.01 – 0.5
Tanning	0.01 – 0.3 and 0.3 – 0.5 (small hides)
Finishing	0.3

Biocides applied in the tannery industry are essentially non-oxidising biocides. They can be categorised as quaternary ammonium compounds, isothiazoles, halogenated organic compounds e.g., Bronopol (2-bromo-2-nitro-propane-1,3-diol), isothiazoles and halogenated organic compounds containing hetero-cycles like derivatives of benzothiazole (IPPC, 2000).

4. RELEASE ESTIMATION.

4.1. Production estimation and water consumption.

4.1.1. Production estimation.

The diversity in plant capacities and technologies makes it difficult to establish a default value for the production of a representative model plant for the whole leather industry. A default value of 15 $t.d^{-1}$ of raw hide is used for the "mass of processed goods per day (W_1)", when no specific data are available, in the emission scenario document for the leather processing industry of the Technical Guidance Document (UBA, 1998; EU, 1996). According to the size of the plant, the production varies from 1 $t.d^{-1}$ up to 60 $t.d^{-1}$ of finished leather for plants with more than 200 employees which is quite unusual, as shown in table 1.

4.1.2. Water consumption.

A distinction has to be made between the rates of water consumption of integrated plants (processing of raw skins to final leather) and plants specialised in processing wet-blue. In the first case, water consumption rates are commonly in the range of 25-80 m^3 per tonne of raw hide (UNEP/IEO, 1994) with a median value of 35 $m^3.t^{-1}$ (EU, 1996). For the plants specialised on "wet-blue", water consumption rates are more between 18 $m^3.t^{-1}$ (EU, 1996) and 25 $m^3.t^{-1}$ (UBA, 1998).

Table 5: Average water consumption and characteristics of wastewater from leather production and finishing (EU, 1996).

Process		**$M^3.t^{-1}$ raw hides**
Beamhouse	*soaking*	6
	liming	9
	unliming and pickling	5
	subtotal	**20**
Tanning	*pickling and chrome tannery*	1
	washing after chrome tannery	1.5
	subtotal	**2.5**
Squeezing the water out		0.5
Wet finishing (grain leather)	*washing*	0.5
	neutralisation	0.3
	washing after neutralisation	0.5
	second tanning, dyeing, to grease	0.3
	washing	0.7
	subtotal	**2.3**
Wet finishing		**1.5**
Squeezing the water out		**0.2**
Cleaning water		**5.0**
Total amount of waste water		**32.0**

4.2. Releases.

Emissions of the tanning industry may be in gaseous, liquid and solid form. Yet, the two main sources of releases of processing chemicals are waste water from washing of shipping containers, machinery, etc., and unused active substances in spent baths (UBA, 1998; EU, 1996).
Main releases occur during curing and finishing.

Note:
Partial degradation of an active substance can occur within the process. This is not considered in this document. If data on degradation within the process are available, they can be taken into account in the release estimation.

4.2.1. Releases during curing.

Waste water emissions*:* The stage of curing prevents hides from deterioration during storage and/or transportation. Usually, the technique employed is salting, yet, biocides can be used as alternatives. They can be applied by spraying or, in most cases, in an immersion bath. Some of these biocides can be released to waste water during the washout. The degree of fixation of biocide has been estimated to about 95%.

Air emissions: air emissions may occur during spraying of the biocide on the hides or skins. However, no further data are available, maybe due to the low utilisation of this technique.

4.2.2. Releases during finishing.

Waste water emissions: the finished leather is susceptible to moulds. The main system of application of biocides is drums (closed systems). The non-fixed biocides are then directly released to waste water (degree of fixation 95%).

Air emissions: there are several potential sources of air emissions in the finishing of tanned leather if organic solvents are used. Yet, non-solvent finishing technologies are now developing very quickly and associated releases are much lower. Spray application of biocide is common nowadays, however a release of more than 30% of the applied material may occur. Gas captures and cleaning procedures are then indispensable to limit air emissions (UNEP/IEO, 1994). Unfortunately, no data are available on those emissions.

4.2.3. Releases during other tanning steps.

Biocides may be applied during other steps of the leather tanning such as soaking, pickling, tanning and dyeing. If drums are the recommended method (because of the closed system), paddles and pits are essential for certain processes such as the first soaking of dried hides and processing of long-wooled skins. Yet, in each case the main release occurs to waste water.

4.2.4 Releases during other life-cycle stages

Releases may occur during other life-cycle stages, e.g. the final use of leather articles and the elimination of leather articles.
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 total release to the atmosphere can be assumed. Furthermore for articles subject to cleaning, substantial releases to waste water can be assumed. 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.
Regarding waste elimination, a generic model for releases from landfills is under development and might be used once the model is available.

4.3. Waste water treatment.

The composition of waste water depends on the types of processes and on the level of water consumption.
The waste water treatment plant (STP) is based on a classical scheme. There are usually several options for each processing unit. The final choice depends on the tannery and on local discharge standards.

The classical scheme is:

– *pre-treatment*: mechanical screening to remove coarse material.
– *primary treatment*: sulphide removal from beamhouse effluents ; chrome removal from tanning effluents ; flow equalisation ; physical-chemical treatment for BOD removal and neutralisation.
– *secondary treatment*, usually biological.
– *tertiary treatment*, including nitrification and denitrification.
– *sedimentation and sludge handling* (UNEP/IEO, 1994).

Biocides are treated in the biological step. STP can be private for a single tannery or be a common structure for several small tanneries as shown in table 6 (CEC, 1992).

Table 6: European treatment plants of tanneries (CEC, 1992).

Countries	Collective STPs	On-site STPs	Urban STPs
Italy	X (about 85%)	X (about 10%)	X (about 5%)
Germany		X	
Netherlands		X	
France		X (large tanneries)	X (small tanneries)
Spain	X	X	

4.4. Release estimation.

A release estimation model is presented below.

The release estimation is performed on a local scale. Releases of biocides may occur at each step of application. Yet, the most important steps seem to be curing and finishing. Most of them are done in drums, releases for each step can then be estimated with the following model.

Table 7: Emission scenario for calculating the releases biocides used as preservatives in the leather industry

Variable/parameter (unit)	Symbol	Unit	Default	S/D/O/P
Input:				
Quantity of treated raw hide per day (cf. section 4.1.1)	$Q_{leather}$	$t.d^{-1}$	15	D
Quantity of active substance applied per ton of leather (cf. table 4)	Q_{active}	$kg.t^{-1}$	5	S/D
Fixation rate (cf. section 4.2.1)	F_{fix}	-	0.95	S/D
Output:				
Local emission of active substance to waste water for one treatment step	$Elocal_{x,water}$*	$kg.d^{-1}$		O
Total local emission of active substance	$Elocal_{tot,water}$	$kg.d^{-1}$		O

*x represents a treatment step (salting, soaking, pickling, tanning, finishing)

Model calculation:

$$Elocal_{x,water} = Q_{leather} \times Q_{active} \times (1 - F_{fix})$$

$$Elocal_{tot,water} = \Sigma\ Elocal_{x,water}$$

4.5. Example of calculation.

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

Biocides can be applied in each of the following steps: salting, soaking, pickling, tanning and finishing. Rates of application are given in table 4.
It can be assumed, in a "worst case" situation, that one and the same biocide is applied in each of those steps.

$Q_{active\_salting} = Q_{active\_soaking} = Q_{active\_pickling} = Q_{active\_tanning} = 5\ kg.t^{-1}$.
$Q_{active\_finishing} = 3\ kg.t^{-1}$.

$F_{fix} = 0.95$.

$Elocal_{salting\_water} = Elocal_{soaking\_water} = Elocal_{pickling\_water} = Elocal_{tanning\_water} = 15 \times 5 \times (100 - 95) / 100 = 3.75\ kg.d^{-1}$.

$Elocal_{finishing\_water} = 15 \times 3 \times (100 - 95) / 100 = 2.25\ kg.d^{-1}$.

The release is $Elocal_{tot\_water} = 4 \times 3.75 + 2.25 = 17.25\ kg.d^{-1}$.

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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 unhaired, when necessary, prior to the tanning process.

Deliming: is the process which removes the lime from hides coming from the beamhouse.

Fleshing: to remove the excess tissue, to impart uniform thickness and to remove muscles or fat adhering to the hide.

Finishing: is the final set of processing steps performed on a tanned hide. These operations follow the retan-colour-fatliquor processes, and include the many dry processes involved in converting the hide into the final tannery product.

Leather: is the 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 even after treatment with water.

Pickling: it is the process to preserve hides from deterioration and to further reduce the pH prior to tanning by using salt and acid. Synthetic fat liquors are added to improve softness.

Retanning: is the process of subjecting a skin, 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: is the process to remove salt and other solids and to remove excess moisture lost during curing.

Wet blue: is a term for a hide or skin which has been subject to the usual beamhouse processes, has been chrome-tanned and left wet, and may now be stored or exported in this state.