DOKUZ EYLUL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APLLIED SCIENCES

WASTE MANAGEMENT IN LEATHER INDUSTRY

by
Seçil KARABAY

February, 2008
IZMIR

WASTE MANAGEMENT IN LEATHER INDUSTRY

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We have read the thesis entitled **"WASTE MANAGEMENT IN LEATHER INDUSTRY"** completed by **SEÇİL KARABAY** under supervision of **PROF. DR. SOL KOHEN ÇELEBİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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WASTE MANAGEMENT IN LEATHER INDUSTRY

ABSTRACT

In this, thesis, the Works and regulation in the world and Turkey about waste of Leather Industry have been scrutinized and comparisons and evaluations were made by being predicated on 2 leather facilities. The facilities are Company A operating in the Menemen Free Leather Zone and Company B operating in Torbalı. The processes followed from raw material or semi- finished form of material, the waste created during the operation process, the recovery processes subjected to the waste and the results are examined separately.

In both facilities, Chrome Tanning Process, the most widespread technique in the world, is used. In Company A, Vegetal Tanning is also used. In Company B only small cattle leather is used while in Company B both small cattle and great cattle leather is processed.

The trim waste in Company A is used as raw material in subsidary companies. The trim and shave waste of the Company B is also used and provide raw materials for various organizations. Thus, some part of the present waste is revaluated and waste amount is decreased in this manner.

Due to the pre- waste treatment, the harm given to nature could be minimized. It is examined that there is no pre- treatment facility in Company A but wastewater is transferred to the pre- treatment facility that exists in the region, through 3 separate channels. There is pre- treatment facility in Company B. The wastewater disposed in the sewer system by both facilities are up to standards of Regulation on Water Pollution Control. The solid waste of the Company A is collected by IDESBAS regularly. The solids waste of Company B is eliminated on site.

There is no cleaner- cut EU decision about leather waste. The regulation Leather waste in Turkey were also scrutinized.

Keywords: Leather, treatment, tanning, regulations, waste.

DERİ ENDÜSTRİSİ ATIKLARININ YÖNETİMİ

ÖZ

Bu tezde Deri Endüstrisi atıkları hakkında Dünya ve Türkiye' deki yönetmelikler ve yapılan çalışmalar incelenmiş ve seçilen 2 deri İşletmesi esas alınarak karşılaştırmalar yapılmıştır. İncelemede yer alan tesisler Menemen Serbest Bölgesi' nde halen faaliyette bulunan A işletmesi ve Torbalı' da faaliyette bulunan B işletmesidir. Bu tesislerde derinin ham ya da yarı işlenmiş halinden itibaren elde edilen son ürüne kadar uygulanan işlemler, işletim aşamasında meydana gelen atıklar atıklara uygulanan arıtım prosesleri ve sonuçları ayrı ayrı incelenmiştir.

Her iki tesiste' de Dünya' da en çok uygulanmakta olan Kromla Tabaklama işlemi kullanılmaktadır. A işletmesinde talebe göre Bitkisel tabaklama da yapılmaktadır. A işletmesinde sadece küçükbaş hayvan derisi kullanılırken işletmesinde hem büyükbaş hem de küçükbaş hayvan derisi işlenmektedir.

A işletmesinden çıkan budama atıkları çeşitli yan kuruluşlarda hammadde olarak değerlendirilmektedir. B işletmesinde hem budama hem de tıraş atıkları değerlendirilmekte olup yine çeşitli kuruluşlara hammadde olarak sağlanmaktadır. Böylece mevcut atıkların bir kısmı değerlendirilip, atık miktarı azaltılmış olmaktadır.

Tesislerde bir ön arıtma olduğundan dolayı çevreye verilen etki aza indirgenmektedir. Menemen Serbest Deri Bölgesi' nde faaliyette bulunan A işletmesi bünyesinde bir ön arıtma tesisi mevcut olmayıp, atıksular 3 ayrı kanalla bölge içerisinde bulunan bir ön arıtma tesisine terfi edildiği gözlemlenmiştir. B İşletmesinde tesis bünyesinde bir ön arıtma tesisi mevcuttur. Her iki arıtımda da kanalizasyona verilen çıkış suyunun kirlilik yükü Türkiye' de bu konuda yayımlanmış olan Su Kirliliği Kontrolü Yönetmeliği' nde bulunan standartlara uyduğu görülmüştür. A işletmesinin atıkları IDESBAS tarafından düzenli olarak toplanmaktadır. B işletmesinin atıkları ise tesis içerisinde çöp depolama alanında toplanarak, bertaraf edilmektedir.

Deri atıkları hakkında Avrupa Birliği' nde alınan net bir karar mevcut değildir. Türkiye' de de Deri atıkları üzerine mevcut yönetmelikler incelenmiştir.

Anahtar Kelimeler: Deri, arıtım, tabaklama, yönetmelik, atık.

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CHAPTER ONE
INTRODUCTION

Today leather production is advancing due to the increase in meat consumption. Even though many animal leathers are used, the most used one is calf leather.

These leathers are used as raw material in many sectors. These sectors are:

- Shoe industry,
- Bag industry,
- Clothing industry, and
- Furnishing and decoration.

Leathers are turned into final products of desirable quality after applying many chemical processes. There are four operating processes applied to leather until it becomes a final product, these are;

- Pretanning Operation (Beamhouse Operation)
- Tanning Operation
- Wet- Finishing Operation
- Finishing Operation

In terms of the chemicals used and the tanning method, a lot of pollution is caused during each operating level. These pollution parameters can be classified as solid, liquid and gas. BOD, COD, sulfide caused by the hair-removing process and Cr (III) caused by chrome tanning method, which is used as an alternative method to alternative and vegetative methods, seriously affect the treatment process. These and other parameters are refined in three basic ways.

- Mechanical treatment

- Effluent Treatment
- Post treatment, Sedimentation and Sludge Handling

(Blackman, A., (2005)) It is possible to minimize the pollution during the treatment process by applying environment-friendly technologies and methods as an alternative to these treatment levels.

- High Exhaustion
- Enzyme in the Dehairing Bath
- Precipitation of Chrome
- Recycling the Dehairing Bath
- Recycling the Chrome Tanning Bath

In this thesis, researches have been carried on the issues such as the processes that are applied until the raw leather becomes a final product, waste products that is produced during these processes, the treatment and/or disposal of these waste products, and environment-friendly (clean) technologies that can be used in leather industry. Two different leather industries have been compared in terms of operation and treatment according to the regulations.

CHAPTER TWO
LEATHER PRODUCTION

2.1 The Leather Industry In Turkey

As being the main raw material of leather products industry, the leather has always been one of the most exceptional products in all around the world. What makes it different form the others is the unique character of its raw material, that is the animal skin, and its production process. The processing of raw animal skin to obtain a material suitable for producing clothing or shoes or other leather goods is a long, hard and difficult process which requires great care and labor.

For that reason, when we mention leather processing industry, we explain an industry having great experience and labor tradition.

Turkey has a strong tradition of processing leather which comes from it' s historical past. In the means of this tradition, today, Turkey is one of the most assertive countries in producing high quality leather products in the world.

Particularly, in processing sheep/goat leather, Turkey has the second place in Europe after Italy and fourth place in the world after Italy, China and India.

Besides, Turkey is the World leader in fur production with an annual processing capacity of 80 million units.

In this industry, which has a production capacity of 400 thousand tons yearly, today, there are 1300 tanneries whose inputs, production processes, process capacities and products are different and employ approximately 20000 people.

Currently active big scale tanneries are located in Tuzla (İstanbul), Çorlu (Tekirdağ), Menemen (İzmir), Uşak, Bursa, Manisa, Gönen (Balıkesir). Beside, little or medium firms can be found in Çanakkale, Isparta, Denizli and Niğde.

The reason for having such high numbers of tanneries today is the export boom realized in the early 1990' s. The boomed demand on the leather and leather products from Russia and other neighbor countries, which have moved to free market economy after the political breakdown of Soviet Union, has resulted in an incredible mobilization in production and investment in Turkey as the leading supplier. During this period, while existing tanneries extended their capacities three, four and even five times, many new tanneries started to operate.

Other attractive feature of leather processing industry in Turkey is that it has an environment friendly and modern production infrastructure.

Today, in 13 Organized Leather Industrial Zones, production is performed in European standards, and through environment friendly, modern methods. The 70 % of leather production activity in Turkey employs environment friendly methods.

In comparison to leather goods production, leather processing sub- industry intensively requires skilled labor even though it has a technology based substructure. In this respect, qualified labor force gains great importance. The industry is moving to a more advantageous position in the international competition area due to the rising in number and improving in educating levels of the schools and the transfer of industry' s inherited experience to these newly graduated ones. It should be noted that, Turkey's one of the most important advantage in this industry is the "know- how" capability cumulated over centuries.

However, although there is a strong tradition of production and existence of high capacity, unfortunately this is not reflected in exportation.

In year 2005, a total of 65 million USD worth of finished leather was exported. The biggest finished leather market countries, according to their market share rates are; 13. 2 % Hong Kong, 9. 8 % Belarus, 9. 5 % Russia, 7. 8 % Romania and 7. 1 % Italy.

On the other hand, in recent years, the industry started to focus more on exportation and as a consequence, important achievements in export performance has realized in various markets, especially in Far East countries' markets like Vietnam, Indonesia and China.

The advantages of Turkish leather processing industry in international competition are:

- Organized industrial zones and environment friendly, technology based production infrastructure
- Ability to produce high quality products with the developed chemical industry
- Flexible production capability
- Production quality above the average level
- The processing of the world' s 22 % small cattle (sheep/goats etc.) leather production is realized in Turkey

[*Turkish Leather Processing Industry* , (n. d.)]

CHAPTER THREE
THE TANNING PROCESS

3.1 Introduction to Leather Process

(*Ecology and Environment in the Leather Industry-Technical Handbook*, (1995)) The production processes in a tannery can be split into four main categories;

a. **Pretanning** (hide and skin storage and beamhouse operations)
b. **Tanning** (tanyard operation)
c. **Wet Finishing** (post- tanning operations), and
d. **Finishing Operations**

An overview on the steps of leather processing is given in Figure 3.1.

3.1.1 Pretanning (Beamhouse Operations)

Cleaning and conditioning hides and skins produce the biggest part of the effluent load.

3.1.1.1 Soaking

The preserved raw hides regain their normal water contents. Dirt, manure, blood, preservatives (sodium chloride, bactericides), etc. are removed. (*Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing*, (2007)) Soaking is usually carried out in processing vessels (e. g. Mixers, drums, pits, or raceways) in two steps, namely a dirt soak for salt and dirt removal, and a main soak. The soak bath is often changed every 8 hours to prevent bacterial growth. Soaking additives include surfactants, enzyme preparations, bactericides, and alkali products.

3.1.1.2 Fleshing and Trimming

(*Ecology and Environment in the Leather Industry-Technical Handbook*, (1995)) Extraneous tissue is removed. Unhairing is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulfide and lime. When after skinning at the slaughterhouse the hide appears to contain excessive meat, fleshing usually precedes unhairing and liming. Liming and unhairing produce the effluent stream with the highest COD value. (*Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing*, (2007)) The fleshing machine consists of rollers and rotating spiral blades that the pelts. Fleshing of green hides after soaking is called 'green fleshing'. Fleshing performed after the liming and dehairing is known as 'lime- fleshing'.

3.1.1.3 Deliming and Bating

(*Ecology and Environment in the Leather Industry-Technical Handbook* (1995)) The unhaired, fleshed and alkaline hide are neutralised with acid ammonium salts and treated with enzymes, similar to those found in the digestive system, to remove hair remnants and to degrade proteins. During this process hair roots and pigments are removed. This results in the major parts of the ammonium load in the effluents.

3.1.1.4 Pickling

Pickling increases the acidity of the hide to a pH value of 3 by addition of acid liquor and salts, enabling chromium tannins to enter the hide. Salts are added to prevent the hide from swelling. For preservation purposes, 0.03- 2% by weight of fungicides and bactericides are usually applied.

3.1.1.5 Degreasing

Normally performed together with soaking, pickling or after tanning, degreasing is performed by organic solvents or surfactants, leading to a higher

COD value in the effluent. [*Ecology and Environment in the Leather Industry-Technical Handbook* , (1995)]

3.1.2 Tanning (Tanyard Operation)

(*Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing*, (2007)) Tanning allows stabilization of the collagen fiber through a cross- linking action. The tanned hides and skins are tradable intermediate products (wet- blue). Tanning agents can be categorized in three main groups namely mineral (chrome) tanning agent; vegetable tanning agents; and alternative tanning agents (e. g. Syntans, aldehydes, and oil tanning agents).

3.1.2.1 Chrome Tanning (CT)

(*Ecology and Environment in the Leather Industry-Technical Handbook*, (1995)) CT is the most common type of tanning in the world. After pickling, when the pH value is low, chromium (III) salts are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross- linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature. Chrome tanned leather are characterized by top handling quality, high hydro- thermal stability, user- specific properties and versatile applicability. Waste chrome from leather manufacturing, however, poses a significant disposal problem.

3.1.2.2 Vegetable Tanning (VT)

(*Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing*, (2007)) ,Vegetable tanning produces relatively dense, pale brown leather that tends to darken on exposure to natural light. Vegetable tanning is frequently used to produce sole leather, belts, and other leather goods. Unless specifically treated, however, vegetable tanned leathers have low hydrothermal stability, limited water resistance, and are hydrophilic.

(*Ecology and Environment in the Leather Industry- Technical Handbook*, (1995)) Vegetable tannins are polyphenolic compounds of two types;

- Hydrolysable tannins (i.e. chestnut and myrobalam) which are derivatives of pyrogallols, and

- Condensed tannins (i.e. hemlock and wattle) which are derivatives from catechol.

3.1.2.3Alternative Tanning

(*Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing*, (2007)) Tanning with organic tanning agents, using polymers or condensed plant polyphenols with aldehydic cross- linkers, can produce mineral-free leather with high hydrothermal stability similar to chrome- tanned leather. However, organic- tanned leather usually is more filled (e. g. leather with interstices filled with a filler material) and hydrophilic than chrome- free leather, with equally high hydrothermal stability. This tanning process is carried out with a combination of metal salts, preferable but not exclusively aluminum (III), and a plant polyphenol containing pyrogallol groups, often in the form of hydrolysable tannins.

3.1.2.4 Draining, Samming, and Setting

After tanning, leather are drained, rinsed, and either hung up to age or unloaded into boxes and subsequently sammed (e. g. brought to a uniformly semi-dry state to reduce the moisture content before further mechanical action. Setting (working over the grain surface of wet leather to remove excess water, to eliminate wrinkles and granulations, to give the leather a good pattern and to work out stresses so that the leather lies flat) may be carried out to stretch out the leather.

3.1.2.5 Splitting

The function of the splitting is to cut through skins/ hides or leathers at a set thickness. If the hide/ skin is sufficiently thick, splitting can yield a grain split and a flesh split that may both be processed into finished leather. Although splitting can be performed before tanning, after tanning, or after drying, it is usually performed after tanning.

3.1.2.6 Shaving

Shaving is undertaken to achieve an even thickness throughout tanned or crusted leather. Shaving is carried out when splitting is not possible or when minor adjustments to the thickness are required.

3.1.3 Wet Finishing (Post- Tanning)

Post- tanning operations involve neutralization and bleaching, following by retanning, dyeing, and fatliquoring. These processes are mostly undertaken in a single processing vessel.

Specialized operations may also be performed to add certain properties to the leather product (e. g. Water repellence or resistance, oleophobicity, gas permeability, flame retardancy, abrasion resistance, ad anti- electrostatic properties).

3.1.3.1 Neutralization

Neutralization is the process by which the tanned hides are brought to a pH suitable for retanning, dyeing and fatliquoring. Neutralization is performed using weak alkalis (e. g. Sodium or ammonium bicarbonate, formiate, or acetate). After neutralization, leather may be dried, generating an intermediate tradable product called white crust.

3.1.3.2 Bleaching

Vegetable- tanned skins and leathers with wool or hair may need to be bleached to remove stains or to reduce the coloring before retanning and dyeing. Making the leather color fade may be achieved using treatment with chemicals (e.g. bleaching agents) or exposure to the sun/ weather elements.

3.1.3.3 Retanning

The retanning process is performed to improve the leather characteristics and the re- wetting properties (e. g .the introduction of liquid, such as water, into hides, skins or dried leather) of the hides necessary to facilitate and optimize the subsequent dyeing process. A wide variety of chemicals may be used for the re-tannage of leather, including vegetable tanning extracts, syntans, aldehydes, resins and mineral tanning agents.

3.1.3.4 Dyeing

Dyeing is performed to produce colors in hides/ skins. Typical dyestuffs include water- based acid dyes. Basic and reactive dyes are less commonly used. A wide range of dyestuff is available with different characteristics and physico-chemical resistance (e. g. to light, PVC migration, sweat migration, among others).

3.1.3.5 Fatliquoring

Fatliquoring is the process by which leathers are lubricated to achieve product- specific characteristics and to reestablish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or may be synthetic products based on mineral oils. Stuffing is an old technique used mainly for heavier vegetable- tanned leather. Sammed leather is treated in a drum with a mixture of molten fat. The retanned dyed, and fatliquored leathers are then acidified by formic acid for fixation and usually washed before being aged to allow the fat to migrate from the surface to the inside of the pelt.

3.1.3.6 Drying

The objective of drying is to dry the leather while optimizing leather quality. Drying techniques include samming, setting, centrifuging, hang drying, vacuum drying, toggle drying (leather dried while held under tension on frame using toggles), paste drying (drying method used for upper leather with corrected grain), and over drying. Samming and setting are used to reduce the moisture content mechanically before implementing another drying technique. After drying, the leather may be referred to as ‘crust’, which is a tradable and storable intermediate product. [*Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing*, (2007)]

3.1.4 Finishing

(*Ecology and Environment in the Leather Industry- Technical Handbook*, (1995)) The crust that results after retanning and drying is subjected to a number of finishing operations. The purpose of these operations is to make the hide softer and to mask small mistake. The hide is treated with an organic solvent on water based dye and varnish. Environmental aspects are mainly related to the finishing chemicals which can also reach effluent water.

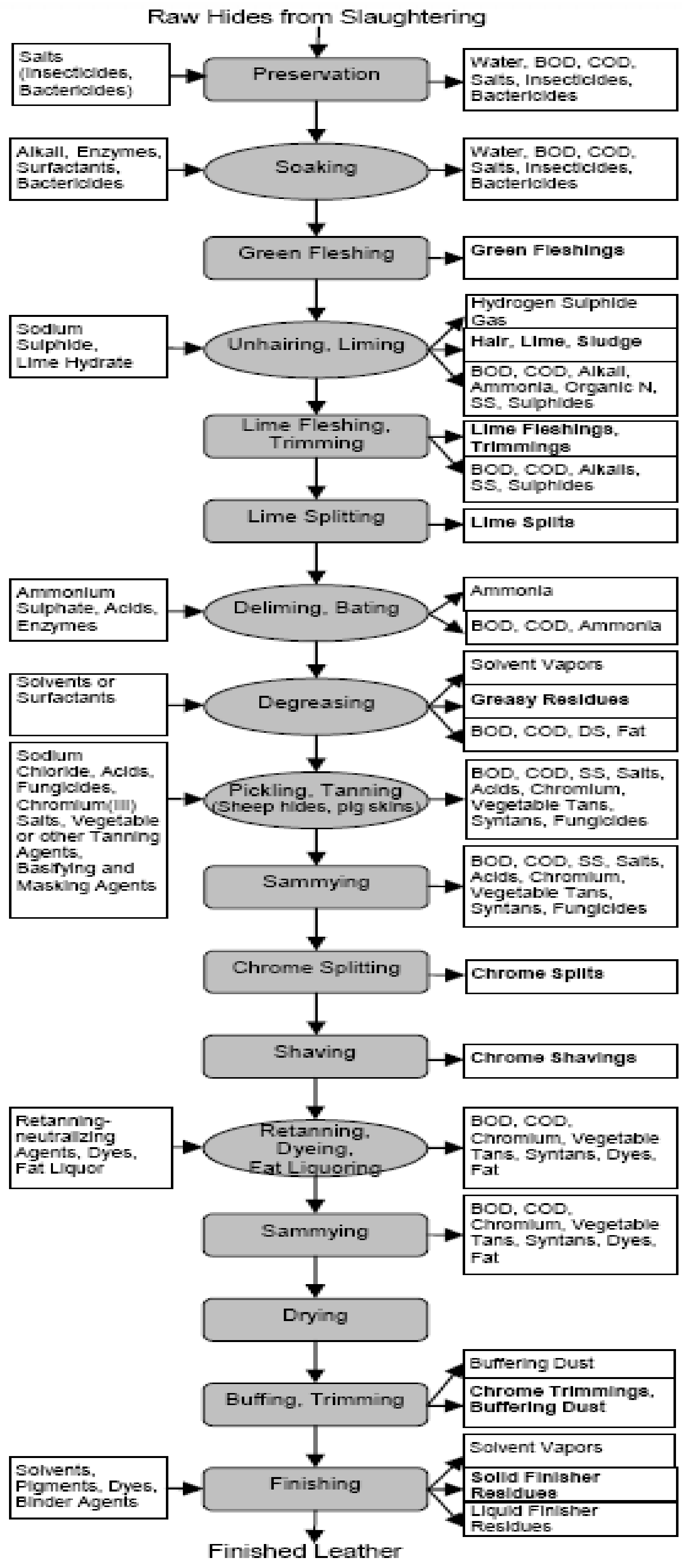


Figure 3.1 An overview on the steps of leather processing

CHAPTER FOUR
CHEMICALS USED IN TANNING PROCESSES

4.1 Processing Chemicals

A variety of chemicals, from common salts (sodium chloride) to the fine finishing chemicals, are used in Leather sector. About 130 different types of chemicals are applied in leather manufacturing, depending on the type of raw material and the end product of the industry. These chemicals are divided into four major classes, described below, as per their use.

4.1.1 Pre- Tanning Chemicals

These chemicals are used to clean and to prepare the skins for the tanning processes. These chemicals do not react with the skins' fiber, therefore are not retained by the skins. These chemicals after performing their respective functions are discharged with the wastewater.

4.1.2 Tanning Chemicals

These tanning chemicals react with the collagen fibers of the skin and convert them into leather. As these chemicals react with the fiber, therefore, a considerable quantity is retained by the fiber. A Nevertheless, a significant amount remains unused and is discharged with the wastewater. Basic chrome sulphate is the tanning chemical, which most widely used in local tanneries. This is an expensive chemical and also poses a serious environmental threat. Besides environmental problems, its discharge into wastewater is also a financial loss. Vegetable tanning materials are also used in local tanneries but their use is not common as compare to chromium.

4.1.3 (Wet) Finishing Chemicals

These chemicals are used to impart certain properties, e. g. appearance, softness, flexibility, color strength, etc. as per the requirement of the finished product. These chemicals also react with the collagen fibers of the tanned leather and again a maximum quantity of the applied chemicals is retained by the skins. Whereas un- reacted or residual chemical is discharged with the wastewater of the process.

4.1.4 Finishing Chemicals

Finishing chemicals are applied as surface coating material to impart the desired surface finish to the leather. Most of the applied quantity is retained by the surface of the leather. However, due to limitations of the application procedure some quantity does go into the waste. [*The Leather Sector*, (1998)]

The tanning industry gives rise to two types of hazard involving chemicals. These are, firstly, those concerning particular chemicals used in the various tanning processes, and secondary, chemical substances produced as by- products by the chemical reactions occurring when a hide undergoes the tanning process.

The first type of hazard includes the vast majority of chemicals to be found in tanning. It is possible to divide these materials into groups based either on the particular degree of hazard they present, or on their chemical nature (e. g. acids, alkalis, etc..)

In the second hazard type defined above the major by- product which presents a chemical hazard to workers is hydrogen sulfide.

In terms of toxicity and potential to cause a hazard it is a relatively straight forward task to divide a typical list of chemicals used in tanning into three groups representing major, moderate, and minor potential hazards that are given in Table 4.1 [*Chemical Handling in Leather Industry*, (2004)]

Table 4.1 Major, Moderate and Potential Hazard in Leather Industry

High Potential Hazard Group					
Acetic Acid	Ammonia	Calcium Hydroxide	Formaldehyde	Formic acid	Glutaraldehyde hydrocloric acid
Hydrogen peroxide	Oxalic acid	Sodium chlorite	Sodium hydroxide (caustic soda)	Sulphuric acid	Sulfides and Hydrosulfides
Moderate Potential Hazard Group					
Aluminium sulphate (as lacquer constituents)	Amyl alcohol (as lacquer constituents)	Benzyl alcohol (lacquer solvent) carbon black	Chromium salts (trivalent) enzymes	Isoproply alcohol perchloroethtlene toluene	White spirit
Low Potential Hazard Group					
Alums	Acetone	Anbumen	Ammonium chloride	Ammonium sulphate	Borax, boric acid
Casein	Calcium Chloride	Castor oil china clay	Ethanol (ethyl alcohol)	Fat liquors	Fats
Ferrous acetate	Ferrous sulphate	Gelatine	Glues	Lactic acid	Lanoline
Lecithin	Oils	Parafin	Pigment dispersions	Sequestering agents	Silicones
Sodium acetate	Sodium bicarbonate	Sodium citrate	Sodium carbonate	Sodium formate	Sodium metabisulphate
Sodium nitrite	Sodium phthalate	Sodium sulphite	Sodium thiosulphate	Synthetic tannins	Tragacanth
Titanium salts	Vegetable tanning extracts		Waves	Wetting agents	

CHARTER FIVE
WASTE CHARACTERISTICS

The potential environmental impacts of tanning are significant. Composite untreated wastewater, amounting to 20- 80 cubic meters per metric ton (m^3/ t) of hide or skin, is turbid, colored, and foul smelling. It consists of acidic and alkaline liquors, with chromium levels of 100- 400 milligrams per liter (mg/ l); sulfide levels of 200- 800 mg/l; nitrogen levels of 200- 1. 000 mg/ l; biochemical oxygen demand (BOD) levels of 900- 6. 000 mg/ l, usually ranging from 160 to 24. 000 mg/ l; chemical oxygen demand (COD) ranging from 800 to 43. 000 mg/ l in separate streams, with combined wastewater levels of 2. 400 to 14. 000 mg/ l; chloride ranging from 200 to 70. 000 mg/ l in individual streams and 5. 600 to 27. 000 mg/ l in the combined stream; and high levels of fat. Suspended solids are usually half of chloride levels. Wastewater may also contain residues of pesticides used to preserve hides during transport, as well as significant levels of pathogens. Significant volumes of solid wastes are produced, including trimmings, degraded hide, and hair from the beamhouse processes. The solid wastes can represent up to 70 % of the wet weight of the original hides. In addition, large quantities of sludges are generated. Decaying organic material produces strong odors. Hydrogen sulfide is released during dehairing, and ammonia is released in deliming. Air quality may be further degraded by release of solvent vapors from spray application, degreasing, and finishing (for example, dye application). [*Tanning and Leather Finishing*, (1998)]

5.1 Pollutants in Tannery Effluents

This research is given by M. Bosnic, J. Buljan and R. P. Daniels (2000), In some instances, liquid waste is discharge into sewage systems (indirect discharge) where it undergoes full- scale treatment before being returned to the environment via surface water.

Where effluent is discharged direct into streams and rivers, it needs to be of higher quality as the environment is sensitive and highly susceptible to damage. The greater the volume of the effluent compared to the volume of surface water, the higher the quality of the effluent demand by the environment.

Discharge limits are set with the objective of protecting the environment. The levels of the different pollution in effluent are determined in two ways. The limits are:

(a) based on standards which have been widely applied and found generally acceptable. This method, however, tends to ignore specific individual situations.

(b) set along the lines of mass- balance, whereby the quality of the water upstream and the quality requirements of the water downstream (for industrial or drinking purposes) are determined. The different between the two figures the tolerance levels at the point of discharge.

The second method takes account of individual site factors. Clearly, a small tannery with a high dilution factor should be seen in more favorable light than a large effluent volume with a relatively lower dilution factor. In the effluent load of a large tannery or group causing considerable damage or a small tannery being unduly penalized for discharging effluent into surface waters despite its good treatment facilities and high dilution factor.

The limits imposed should always relate to volume of effluent and the total weight of pollutants. If better housekeeping reduce the volume of water used, thus increasing the concentration, the limits can be reasonable relaxed.

The effect of excessive pollutant levels commonly found in tannery effluent can be severe; their impact is described below for guidance. The main problems presented by those components are summarized together with and outline of the methods.

5.1.1 Solids

The solids to be found in tannery effluent fall into several distinct categories.

5.1.1.1 Suspended Solids

The suspended solids components of an effluent is defined as a quantity of insoluble matter contained in the wastewater. These insoluble material cause a variety of problems when discharge from a site; essentially, they are made up of solids with two different characteristics.

5.1.1.1.1 Solids With A Rapid Settling Rate (Settleable Solids): Settleable solids comprise material that can be seen in suspension when an effluent sample is shaken, but settle when the sample is left to stand. The majority of these solids settle within 5 to 10 minutes, although some fine solids require more than an hour to settle.

These solids originate from all stages of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors. Large volumes are generated during beamhouse processes.

If the waste waters are to be treated in sewage works or undergo traditional effluent treatment, the main problems that arise are due to the large volume of sludge that forms as the solids settle. Sludge often contains up to 97 % water, giving rise to huge quantities of ‘light’ sludge. Even viscous sludge has a water content of around 93 %, and can easily block sumps, sludge pumps and pipes. All this sludge has to be removed, transported, dewatered, dried and deposited, thus placing an inordinate strain on plant, equipment and resources.

If the wastewater is to be discharged into surface water, the rate of flow will determine the distance the material is carried before settling on the stream or river bed.

Even thin layer of settled sludge can form a blanket that deprives section of the river or lake bed of oxygen. Plant and aquatic life dies and decomposition set in.

5.1.1.1.2 Semi- Colloidal Solids: Semi- colloidal solids are very fine solids that, for all practical purposes, will not settle out from an effluent sample, even after being left to stand for a considerable period of time. They can, however, be filtered from solution. Together with the more readily settleable solids, they thus comprise the suspended solids of an effluent that can be measured analytically.

Most of these solids are protein residues from the beamhouse operations- mainly liming processes; however, large quantities are also produced owing to poor uptake in vegetable tanning processes, another source being poor uptake during retanning.

Semi- colloidal solids will not directly cause a sludge problem. They can be broken down over an extended period by bacterial digestion and they produce solids, which will eventually settle.

5.1.2.1 Settleable Solids

Although suspended solids analysis is the method most commonly used to assess insoluble matter, analysis of the settleable solids content is sometimes required. The settleable solids content is determined by leaving the shaken sample to settle and then filtering a known volume of the semi- colloidal matter remaining in suspension. After drying and weighing, the quantity of semi- colloidal matter can be calculated.

5.1.3.1 Gross Solids

Gross solids are large than a sampling machine can handle, hence they are not measured. Their presence, however, is clear to see and the dangers they pose are fully recognized.

The waste components that give rise to this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags. They can be easily removed by means of coarse bar screens set in the wastewater flow. If, however, they emerge from the factory, they settle out very rapidly.

5.1.2 Oxygen Demand

Many components in effluent are broken down by bacterial action into more simple components. Oxygen is required for both the survival of these bacteria (aerobic bacteria) and the breakdown of the components. Depending on their composition, this breakdown can be quite rapid or may take a very long time.

In effluent with a high oxygen demand is discharged directly into surface water, the sensitive balance maintained in the water becomes overloaded. Oxygen is stripped form the water causing oxygen dependent plants, bacteria, fish as well as the river or stream itself to die. The outcome is an environment populated by non- oxygen dependent (anaerobic) bacteria leading to toxic water conditions.

Under normal working condition, both water and carbon dioxide are produced in large volumes; the process, however, depends upon bacteria growth. As the bacteria die, they form sludge that has to be treated and ultimately disposed of. This sludge has high water content and is often quite difficult to dewater, thus adding considerably to the treatment costs.

In order to assess an effluent' s impact on discharge to surface waters or determine the costs of treatment, the oxygen demand needs to be determined. This can be achieved in two different ways:

5.1.2.1 Biochemical Oxygen Demand (BOD5)

The BOD_5 analysis, generally termed BOD, is widely used to assess the environmental demands of wastewater. This methods of detection has various weaknesses: the bacterial cultures can vary and the analysis is a highly sensitive process. If the most stringent care is not taken during the preparation and the analysis itself, the results can be misleading.

It should also be remembered that although BOD is a measure of the oxygen reqirements of bacteria under controlled conditions, many effluent components take longer than the period of analysis to break down. Some chemicals will only be partially broken down, while others may not be significantly affected. Typically, vegetable tanning wastes have a long breakdown period, often quoted as being up to 20 days. These longer digestion periods can apply to a variety of the chemicals used in manufacturing leathers, including certain retanning agents, some synthetic fatliquors, dyes and residual proteins from hair solubilization.

This longer breakdown period means that the environmental impact is spread over a larger area as the wastewater components are carried greater distances before breaking down.

5.1.2.2 Chemical Oxygen Demand (COD)

COD is often favored as it provides rapid results (hours as opposed to days). It is more reliable and cost effective as it is easier to manage large numbers of samples.

The results are always higher than those obtained using the BOD_5 analysis. As a rule of thumb, the ratio between COD: BOD is 2. 5: 1, although in untreated effluent samples variations can be great as 2: 1 and 3: 1. This depends on the chemicals used in the different leather making processes and their rate of biodegradability.

It should be noted that both techniques are based on settle effluent, not filtered. The semi- colloidal material that forms part of the suspended solids is also included in the BOD and COD determinations. Normally 1 mg/ l suspended solids will generate a COD increase of approximately 1. 5 mg/ l.

5.1.3 Nitrogen Compounds

Nitrogen is contained in several different components in tannery effluent. Sometimes these sources have to be differentiated.

5.1.3.1. Total Kjeldahl Nitrogen (TKN)

Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common chemicals are ammonia (from deliming materials) and the nitrogen contained in proteinaceous materials (from liming/ unhairing operations).

These sources of nitrogen pose two direct problems.

1. Plants require nitrogen in order to grow, but the high levels released by substances containing nitrogen over- stimulate growth. Water- based plants and algae grow too rapidly, whereupon waterways become clogged and flows are impaired. As the plants die, a disproportionately high amount of organic matter has to be broken down. If the load outstrips the natural supply of oxygen from the river, plants, fish and aerobic bacteria die and ultimately anaerobic conditions develops.

2. The nitrogen released through protein breakdown and the deliming process is in the form of ammonia. The latter can be converted by bacteria over several stages into water and nitrogen gas which is ultimately released into the atmosphere. Both of these breakdown products are non- toxic, yet large volumes of oxygen are needed in the process. If oxygen demand is greater than the level supplied naturally by the water course, toxic anaerobic is conditions can rapidly develop.

The nitrogenous compounds can be broken down by combining intensive aerobic and anoxic biological treatment. The oxygen demand is very high, thus leading to correspondingly high operation and energy costs. The compounds containing nitrogen can be determined by the Kjeldahl method of analysis.

5.1.3.2 Ammonium Content As Nitrogen (N)

Often confused with TKN, this value is sometimes require in discharge limits and. As ammonium compounds are part of TKN, the problems associated with rapid plant growth and oxygen demand are the same. These compounds are mostly the outcome of the deliming process, with comparatively small volumes being produced from liming and unhairing. The analysis is similar to TKN, but omits the initial digestion stage. This excludes the nitrogen component resulting from protein wastes.

5.1.4 Sulfides

(*Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing*, (2007)) Sulfides are used in the dehairing process. Hydrogen sulfide (H_2S) may be released when sulfide- containing liquors are acidified and during normal operational activities (e.g. opening of drums during the deliming process, cleaning operations/ sludge removal in gullies and pits, and bulk deliveries of acid or chrome liquors pumped into containers with solutions of sodium sulfide). Hydrogen sulfide is an irritant and asphyxiant.

5.1.5 Neutral salts

Two common types of salts are to be founding tannery effluent.

5.1.5.1 Sulphate

Sulphates are a component of tannery effluent, emanating from the use of sulphuric acid or products with a high (sodium) sulphate content. Many auxiliary chemicals contain sodium sulphate as a by- product of their manufacture. For example, chrome tanning powders contain high levels of sodium sulphate, as do many synthetic retanning agents.

An additional source is created by removing the sulfide component from effuent by aeration since the oxidation process creates a whole range of substances, including sodium sulphate. These sulphates can be precipitated by calcium- containing compounds to form calcium sulphate which has a low level of solubility.

Problems arise with soluble sulphates, however, for two main reasons:

1. Sulphates cannot be removed completely from a solution by chemical means. Under certain biological conditions, it is possible to remove the sulphate from a solution and bind the sulphur into microorganisms. Generally, however, the sulphate either remains as sulphate or is broken down by anaerobic bacteria to produce malodorous hydrogen sulfide. This process occurs very rapidly in effluent treatment plants, sewage systems and water courses, if effluents remain static.

This bacteria conversion to hydrogen sulfide in sewage systems results in the corrosion of metal parts, and unless sulphate- resistant concrete will gradually erode.

2. If no breakdown occurs, the risk of increasing the total concentration of salts in the surface water and groundwater runs is incurred.

Sulphate analysis is performed by adding barium chloride solution to a sample of filtered effluent. The sulphates are precipitated as barium sulphate and filtration; drying and calculation can determine the sulphate level.

5.1.5.2 Chlorides

Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment. Considerable quantities of salts are produced by industry and levels can rapidly rise to the maximum level acceptable for drinking water. Increased salt content in groundwater, especially in areas of high industrial density, is now becoming a serious environmental hazard.

Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases through evaporation and crop yields fall. When flushed from the soil by rain, chlorides re- enter the eco- system and may ultimately end up in the ground water. High salt content are only acceptable if the effluents are discharge into tidal/ marine environments.

The level of salt as chloride under acid conditions can be determined by titration a known volume of effluent with a silver nitrate solution, using potassium chromate as an indicator. Under neutral or alkaline conditions, excess silver nitrate is added. This excess is then determined by retro- titration with potassium thiocyanate, using ferric alum as the indicator.

5.1.6 Oils And Grease

During leather manufacture, natural oils and grease are released from within the skin structure. If fat liquor exhaustion is poor, some fatty substances may be produced through inter- reaction when wastewaters mingle.

Floating grease and fatty particles agglomerate to form 'mats' which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems. If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If these fatty substances emulgate, they create a very high oxygen demand on account of their bio- degradability.

The presence of oils and grease is determined by shaking the effluent sample with a suitable solvent and allowing the solvent to separate into a layer on top of the effluent. This solvent dissolves fatty matter, and a quantity can be drawn off and evaporated until dry. The residual grease can be weighed and calculated.

5.1.7 pH Value

Acceptable limits for the discharge of wastewaters to both surface waters and sewers vary, ranging between from pH 5. 5 to 10. 0. Although stricter limits are often set, greater tolerance is shown toward higher pH since carbon dioxide from the atmosphere or from biological processes in healthy surface water systems tends to lower pH levels very effectively to neutral conditions. If the surface water pH shifts too far either way from the pH range of 6. 5- 7. 5, sensitive fish and plant life are susceptible to loss.

Municipal and common treatment plants prefer discharges to be more alkaline as it reduces the corrosive effect on concrete. Metals tend to remain insoluble and more inert, and hydrogen sulfide evolution is minimized. When biological processes are included as part of the treatment, the pH is lowered to more neutral conditions by carbon dioxide so evolved.

5.1.8 Chrome (Trivalent Chrome, Chrome III)

Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the retanning system and is displaced from leathers during retanning and dyeing processes.

This chrome is discharged from processes in soluble form; however, when mixed with tannery wastewater form other processes (especially if proteins are present), the reaction is very rapid. Precipitates are formed, mainly protein-chrome, which add to sludge generation.

Very fine colloids are also formed which are then stabilized by the chrome- in effect, the protein has been partially tanned. The components are thus highly resistant to biological breakdown, and the biological process in both surface waters and treatment plants is inhibited.

Once successfully broken down, chromium hydroxide precipitates and persists in the ecosystem for an extended period of time.

If chrome discharges are excessive, the chromium might remain in the solution. Even in low concentrations, it has a toxic effect upon daphnia, thus disruption the food chain for fish life and possibly inhibiting photosynthesis.

Chrome levels can be determined in a number of ways. The first stage, however, usually comprises boiling a known volume of sample with concentrated nitric acid to ensure complete solution of the chrome. After suitable dilution, the chromium level is determined by atomic absorption. Where high levels of chrome are expected, iodine/ thiosulphate titrations are sometimes used. That technique, however, is inaccurate at low concentrations.

5.1.9 Other Metals

Other metals which might be discharged from tanneries and whose discharge may be subject to statutory limits include aluminum and zirconium.

Depending on the chemical species, these metals have differing toxicities that are also affected by presence of the other organic matter, complexing agents and the pH of the water. Aluminum, in particular, appears to inhibit the growth of green algae and crustaceans are sensitive to low concentrations. Cadmium, sometimes used in yellow pigments, is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms.

5.1.10 Solvents

Solvents originate from degreasing and finishing operations. Solvents in effluents discharged to surface waters can form a microfilm on the water surface, thus inhibiting the uptake of oxygen. Solvents break down in a variety of ways; some inhibit bacterial activity and remain in the eco- system for extended periods of time. Analysis is highly specialized.

A healthy river can tolerate substances with low levels of oxygen demand. The load created by tanneries, however, is often excessive, and the effluent requires treatment prior to discharge. This is often achieved by using bacteria in a properly operated effluent treatment plant: a process demanding high levels of oxygen. Oxygen induction can be achieved by blowing large volumes of air into the effluent: a process entailing a high- energy demand and, as a corollary, high capital and operational costs.
[Bosnic, M., Buljan, J., and Daniels, R. P., (2000)]

5.1.11 Air Emissions

(*The Leather Sector*, (1998)), Hydrogen sulfide and ammonia are the major gases emitted during the washing of the drum with ammonia, effluent of de-liming agent, and mixing of tanning and de- liming effluent. For these reasons, samples of air were colleted of air were collected from the liming section and tanyard/ dyeing section.

5.2 Pollution Prevention And Control

The design of new plants should address the following process modifications:

- Process fresh hides or skins to reduce the quantity of salt in wastewater, where feasible.
- Reduce the quantities of salt used for preservation. When salted skins are used as raw material, pre-treat the skins with salt elimination methods.
- Use salt or chilling methods to preserve hides instead of persistent insecticides and fungicides.
- When antiseptics/biocides are necessary, avoid toxic and less degradable ones especially those containing arsenic, mercury, lindane, pentachlorophenol or other chlorinated substances.
- Fleshing of green hides instead of limed hides.
- Use sulfide and lime as a 20-50% solution to reduce sulfide levels in wastewater.
- Split limed hides to reduce the amount of chrome needed for tanning.
- Consider the use of carbon dioxide in deliming to reduce ammonia in wastewater.
- Use only trivalent chrome when required for tanning.
- Inject tanning solution in the skin using high pressure nozzles and implement chrome recovery from chrome containing wastewaters which should be kept segregated from other wastewaters. Recycle chrome after precipitation and acidification. Improve fixation of chrome by addition of dicarboxylic acids.

- Recycle spent chrome liquor to the tanning process or to the pickling vat.
- Examine alternatives to chrome in tanning, such as titanium, aluminum, iron zirconium, and vegetable tanning agents.
- Use non organic solvents for dyeing and finishing.
- Recover hair by using hair saving methods (for example, avoid dissolving hair in chemical both by proper choice of chemicals and use screens to remove them from wastewater) to reduce pollution loads.
- Use photocell assisted paint spraying techniques to avoid over spraying.
- Precondition hides before vegetable tanning.

Through good management, water use can be reduced by 30-50% to 25 liters per kilograms (L/kg) of raw material. Actions to reduce water consumption should include the following:

- Monitoring and control of process waters–reductions of up to 50% can be achieved.
- Batch washing instead of continuous washing -- reductions of up to 50%.
- Use low float methods such as having 40-80% floats. Recycle liming, pickling, and tanning floats. Recycle sulfide in spent liming liquor after screening to reduce sulfide losses (say by 20-50%) and lime loss (say by 40-60%).
- Use of drums instead of pit for immersion of hides.
- Reuse of wastewaters for washing—for example, by recycling lime wash water to the soaking stage. Reuse treated wastewaters in the process to the extent feasible (such as in soaking and pickling).

Waste reduction measures should include the following:

- Recover hide trimmings for use in the manufacture of glue, gelatin, and similar products.
- Recover grease for rendering. Use aqueous degreasing methods.
- Recycle wastes to the extent feasible in the manufacture of fertilizer, animal feed, and tallow provided the quality of these is not compromised.
- Use tanned shavings in leather board manufacture.
- Control odor problems by good housekeeping, such as minimal storage of flesh trimmings and organic material.

- Recover energy from the drying process to heat process water. .[*Tanning and Leather Finishing,* (1998)]

CHAPTER SIX
WASTE TREATMENT OF TANNERY

Tanning industry is one of the oldest industries of the world and the problem of treatment and disposal of these wastes is probably as old as the industry itself.

Tanneries wastewater effluent is treated in many different ways. There are situations in which an individual tannery applies all the below- described wastewater treatment steps on site. In other situations an individual tannery may apply (on site) only pre- treatment or no treatment at all, sending the effluent to a centralized effluent treatment plant. Nevertheless, a treatment is necessary due to the wide range of toxic effects on the environment caused by untreated tannery effluents and sludges.

The following treatment steps are necessary and will be described in more detail afterwards;

- Mechanical treatment
- Effluent treatment
- Post- purification, sedimentation and sludge handling [*Treatment of Tannery Wastewater*, (2002)]

6.1 Mechanical Treatment

Usually the first treatment of the raw effluent is the mechanical treatment that includes screening to remove coarse material. Up to 30- 40 % of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, Grease, oils, and gravity settling. After mechanical treatment, physical- chemical treatment is usually carried out, which involves the chrome precipitation and sulfide treatment.

Coagulation and flocculation are also part of this treatment to remove a substantial percentage of the COD (Chemical Oxygen Demand) and SS (Suspended Solid).

Effluent from tanneries after mechanical and physical- chemical treatment is generally easily biodegradable in standard aerobic biological treatment plants. Table 6.1 summarizes the pollution loads discharged in effluents from individual processing operations during the tanning process.

Table 6.1 Summary of pollution loads discharged in effluents from individual processing operations (C- conventional technology, A- advantaced technology) [Environmental Commision of IULTCS: Typical Pollution Values Related to Convertional Tannery Processes, London 1997]

Operation	Techno-logy	Pollution load (kg/t raw hide)								
		SS	COD	BOD_5	Cr	S^{2-}	NH_3-N	TKN	Cl^-	SO_4^{2-}
Soaking	C	11-17	22-33	7-11	-	-	0.1-0.2	1-2	85-113	1-2
	A	11-17	20-25	7-9	-	-	0.1-0.2	1-2	5-10	1-2
Liming	C	53-97	79-122	28-45	-	3.9-8.7	0.4-0.5	6-8	5-15	1-2
	A	14-26	46-65	16-24	-	0.4-0.7	0.1-0.2	3-4	1-2	1-2
Deliming, Bating	C	8-12	13-20	5-9	-	0.1-0.3	2.6-3.9	3-5	2-4	10-26
	A	8-12	13-20	5-9	-	0-0.1	0.2-0.4	0.6-1.5	1-2	1-2
Tanning	C	5-10	7-11	2-4	2-5	-	0.6-0.9	0.6-0.9	40-60	30-55
	A	1-2	7-11	2-4	0.05-0.1	-	0.1-0.2	0.1-0.2	20-35	10-22
Post-Tanning	C	6-11	24-40	8-15	1-2	-	0.3-0.5	1-2	5-10	10-25
	A	1-2	10-12	3-5	0.1-0.4	-	0.1-0.2	0.2-0.5	3-6	4-9
Finishing	C	0-2	0-5	0-2	-	-	-	-	-	-
	A	0-2	0	0	-	-	-	-	-	-
Total	C	83-149	145-231	50-86	3-7	4-9	4-6	12-18	137-202	52-110
	A	35-61	96-133	33-51	0.15-0.5	0.4-0.8	0.6-1.2	5-8	30-55	17-37

COD Chemical Oxygen Demand, BOD_5 Biological Oxygen Demand (in five days), SS Suspended Solids, TKN Total Kjeldahl Nitrogen

6.2 Effluent Treatment

In order to carry out effluent treatment in the most effective manner, flow segregation (i. e. keeping wastewater effluents from different process steps separate in order to avoid mixing of different pollutants or dilution of highly polluted streams.) is useful to allow preliminary treatment of concentrated wastewater streams, in particular for sulfide- and chrome- containing liquors. And although a reduction of water consumption dose not reduce the load of many pollutants, concentrated effluents are often easier and more efficient to treat. Where segregation of flows is possible, through mixing of chrome- bearing effluents and other effluent streams improves the efficiency of the effluent treatment plant because the chromium tends to precipitate out with the protein during pretreatment.

The sulfides in the deliming and pickling liquors can easily be oxides in the drum adding hydrogen peroxide, sodium metabisulphite or sodium bisulphite. The associated emission level after treatment of sulfide is 2 mg/ l in a random sample in the separate effluent. Where segregation of sulfide- bearing liquors is not possible, the sulfides are generally removed by means of precipitation with iron (II) salts and aeration.
[*Treatment of Tannery Wastewater*, (April 2002), from Protrade/GTZ "Ecology and Environment in the Leather Industry- Technical Handbook", Eschborn, 1995,]

6.2.1 Activated Sludge

During a biological treatment by activated sludge, the wastewater to be treated is introduced into a bank aerated by mechanical stirring or by compressed air. Here it mixes with the mass of bacteria flock maintained constantly in suspension. After sufficiently contact time, the mixture is clarified in a settling pond and sludge is recycled in an aeration tank. The excess sludge from the system is treated with primary sludge.

6.2.2 Aerated Lagoons

An aerated lagoon is an earthen basin in which the oxygen required by the process is supplied by surface aerators. In an aerobic lagoon, all the solids are maintained as suspension.

6.2.3 Facultative Ponds

Ponds in which the stabilization of waste is brought about by a combination of aerobic, anaerobic and facultative bacteria, are known as Facultative (anaerobic-aerobic) Stabilization Ponds. Three zones exist in a Facultative Ponds:

- a surface zone where bacteria and algae exist in a symbiotic relationship;
- an anaerobic bottom zone in which accumulated solids are decomposed by anaerobic bacteria; and
- an intermediate zone that is partly anaerobic, in which the decomposition of organic waste is carried out facultative bacteria.

Conventional facultative ponds are earthen basins filled with wastewater. In this pond, large solids settle out to form an anaerobic sludge layer. Soluble and colloidal organic materials are oxidized by aerobic and facultative bacteria, using bacteria produced by algae growing near the surface. Carbon dioxide produced in organic oxidation serves as carbon source for the algae. Anaerobic breakdown of the solids in the sludge layer results in the production of dissolved organic compounds and gases such as carbon dioxide, hydrogen sulfide and methane, which are either oxidized by the aerobic bacteria or vented to the atmosphere. In practice, oxygen is maintained in the upper layer of the facultative lagoon by the presence of algae and by surface aeration. In some cases, surface aerators have also been used. If surface aerator is used, algae are not required.

6.2.4 Anaerobic Lagoon

Typically, an anaerobic lagoon is a deep earthen pond with appropriate inlet and outlet piping to converse heat energy and to maintain an anaerobic condition. Anaerobic lagoons are constructed with depths of up to 30 ft. The waste that is added in the lagoon settles down at the bottom. The partially clarified effluent is usually discharged to another process for further treatment.

Usually, these ponds are anaerobic throughout the depth, except for an extremely shallow surface zone. Stabilization is brought about by the combination of precipitation and the anaerobic conversion of organic waste into carbon dioxide, methane, other gaseous end products, organic acids ad cell tissue. Conversion efficiencies of BOD up to 70% can be achieved.

6.2.5 Trickling Filter

The working principle of the trickling filter is by percolating the water to be treated through a mass of porous or cavernous material, which serves as support for micro- organisms. The necessary oxygen required for maintaining an aerobic state for fixing the biomass to the support is generally supplied by natural ventilation. Due to natural ventilation, aeration cost is not required. Tanneries are discharging wastewater containing 40 times more BOD value as compared to domestic wastewater. Nitrification is possible in this type of technology whereas denitrification of wastewater is not possible. Therefore, it is not possible to apply this technology for the treatment of wastewater of tanneries. However, it is a very simple technology and operation and maintenance cost is also very low as compared to the activated sludge technology. A small land area is required for this technology.

6.2.6 Up Flow Anaerobic Sludge Blanket (UASB) Technology

As it is evident from its name, this is an anaerobic process based technology. This treatment system is based on the upward flow of wastewater through a sludge layer of active anaerobic microorganisms. The wastewater is evenly distributed at the bottom of the reactor it leaves from the system from top of the reactor. The contact between the microorganisms of the wastewater is enhanced by the production of biogas, due to the rising bubbles which provide gentle mixing. There is no need for mechanical mixing. This simplifies the design of the reactor. After passing through the sludge bed, a mixture of biogas, sludge and water enters a three phase separator. The biogas is separated in a gas collector, whilst the sludge-water mixture enters a settling compartment, thus providing effective sludge retention in the reactor. The effluent is discharged from the top of the reactor via an overflow weir. The excess sludge is discharged from the bottom of the reactor at the regular intervals onto a drying bed. [*The Leather Sector*, (1998)]

6.3 Post- Purification, Sedimentation and Sludge Handling

(*Ecology and Environment in the Leather Industry- Technical Handbook*, (1995)) Post- purification, sedimentation and sludge handling are the last step in wastewater treatment. With sedimentation the sludge in the wastewater treatment plant is separated from the water phase by gravity settlement. After dewatering this sludge by means of filter presses, a sludge cake with up to 40 % dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20- 25 % dry solids. Centrifuges achieve up to 25- 45 % dry solids and thermal treatment up to 90 % dry solids. Energy is an important factor in these processes.

6.4 Emissions and Controls

There are several potential sources of air emissions in the leather tanning and finishing industry. Emissions of VOC may occur during finishing processes, if organic solvents are used, and during other processes, such as fatliquoring and drying. If organic degreasing solvents are used during soaking in suede leather manufacture, these VOC may also evaporate to the atmosphere. Many tanneries are implementing water- based coatings to reduce VOC emissions. Control devices, such as thermal oxidizers, are used less frequently to reduce VOC emissions. Ammonia emissions may occur during some of the wet processing steps, such as deliming and unhairing, or during drying if ammonia is used to aid dye penetration during coloring. Emissions of sulfides may occur during liming/ unhairing and subsequent processes. Also, alkaline sulfides in tannery wastewater can be converted to hydrogen sulfide if the pH is less than 8.0, resulting in release of this gas. Particulate emissions may occur during shaving, drying, and buffing; they are controlled by dust collectors or scrubbers.

Chromium emissions may occur from chromate reduction, handling of basic chrome sulfate powder, and from the buffing process. No air emissions of chromium occur during soaking or drying. At plants that purchase chromic sulfate in powder form, dust containing trivalent chromium may be emitted during storage, handling, and mixing of the dry chromic sulfate. The buffing operation also releases particulates, which may contain chromium.[*Leather Tanning*,(n. d.)]

6.4.1 Nitrogen Removal

(*Tanwater- Reduction of Nitrogen Discharge from the Leather Industry LIFE03 ENV/S/000595*, (n.d.))The nitrogen is present in the wastewater mainly ammonia. The nitrogen removal is a biological process performed by two processes: nitrification and denitrification. In the first biological process the ammonia nitrogen is oxidized into nitrate. This process takes place under aerobic conditions, i.e. in the presence of oxygen. The process equations are given below (1). In the second process (denitrification), the nitrate is reduced to gaseous nitrogen, which escapes into the surrounding atmosphere. The denitrification takes place under anoxic condition, which means that oxygen is not present or in anoxic zones of the flocks. This process equation is given below (2). In this system, the combination of aerobic and anoxic conditions (which is necessary for the nitrogen removal) is created by switching off the aeration when denitrification is taking place.

(*Wastewater Management Fact Sheet*, (2007))

Nitrification(1):

$NH_3 + O2 \rightarrow NO2 + 3\ H + 2\ e$

$NO2 + H2O \rightarrow NO3 + 2\ H + 2\ e$

Denitrification(2):

$6NO_3 + 2\ CH_3OH \rightarrow 6NO_2 + 2\ CO_2 + 4H_2O$
$6NO_2 + 3\ CH_3OH \rightarrow 3\ N_2 + 3\ CO_2 + 3\ H_2O + 6\ OH$

Overall
$6NO_3 + 5\ CH_3OH \rightarrow 5\ CO_2 + 3\ N_2 + 7\ H_2O + 6\ OH$

6.4.2 Control Of Hydrogen Sulfide As A Tanning By- Product

The dehairing of hides is a necessary tanning process most conveniently achieved by the chemical methods of dissolving the hair by the addition of suitable caustic chemicals. Sulfides, hydrosulfides and lime are the traditional dehairing agents and following treatment with these substances the hides absorbs and retains a proportion of them. Later pickling treatment with sulphuric acid prior to chrome tanning gives rise to hydrogen sulfide by reaction of the retained sulfide and hydrosulfide with the acid. Thus if the traditional tanning processes are continued the production of hydrogen sulfide is inevitable.

In terms of control of the problem there are two alternatives, the first of these being to removed the hydrogen sulfide by efficient ventilation at the source of production, and the second to use a modified chemical process which produces either less or ideally zero hydrogen sulfide, without detriment to the tanning process itself.

6.4.2.1 Ventilation

Suggestions for suitable ventilation can be made as follows, assumption the tanning process is being carried out by the drum method.

- The take- off point for ventilation attached to the tanning drum may be either the drum hatch, which requires stopping the motion and connecting and disconnecting the ducting before opening the hatch; or alternatively by way of a suitable connecting point on the liquid feed- in assembly at the drum axle hub. This latter methods does not require drum motion to halt and in fact provides continuous extraction.

- Ducts, fan blades, etc. must be of acid- resistant material (e.g. PVC) because considerable acid mist is also evolved in the tanning process.

- The duct from should lead into a main ducting shaft, which in turn leads outside the factory and discharge the pollutants at a suitable height. A scrubbing system may be necessary to ensure that the final emissions.

6.4.2.2 Chemical Modification

Chemical modification to the typical methods of pelts processing can lead to substantial reductions in hydrogen sulfide emissions. These modifications centre on the controlled addition of hydrogen peroxide which oxidies residual sulfide to elemental sulphur, and under certain condition to sulphate.

- The hydrogen peroxide should be added at the commencement of the deliming/ bating cycle since this will eliminate the possible emission of hydrogen sulfide if the solution pH momentarily reduces to around 7 at the surface of the pelt. (*Chemicals Handling in the Tanning Industry*, (2004))

(Langlais, R. J., Sayers R. H., (1977)) Sulfide can also be removed by the oxidation of the sulfide to sulfate by air using a manganese sulfate catalyst. In this system the sulfide bearing waste is placed in a tank, manganese sulfate is added as a catalyst, and the waste are aerated for four to six hours. This system is conducted on a batch basis.

6.5 Environmentally Clean Technologies

(*The Leather Sector*, (1998)) A number of cleaner technologies can be applied for the manufacturing of finishing leather. The implementation of cleaner production processes and pollution prevention measure can provide both economic and environmental benefits. However, the applicability of these technologies vary from tannery to tannery due to the varying nature of raw material, processing conditions and the type of finishing leather. Some of the cleaner technologies have been described in Table 6.1.

Table 6.1 Cleaner Technologies

Cleaner Technologies	Benefits
Water Conservation	The use of pit or paddle for soaking operations results in a higher consumption of water, mainly for washing phase which are much less efficient than when using drums. Even for drums it is recommended to operate the sequential washing instead of continuous washing which leads to the savings of enormous amount of water at each stage. Low float technologies would also reduce the water quantity. Although such conservation do not reduce the pollution load, however, they can lead to the reduction in the size of the effluent treatment plant
Use of environment friendly chemicals	Enzymatic product are considered to be less toxic and can be a good replacement of sulphide. Surfactants, if used, should be selected with respect to their biodegradability. Use of Penta Chloro Phenol (PCP) must be avoided. Replacement of ammonium sulphate with weak acids (organic). Degreasing with surfactants instead of organic solvent. Use of trivalent chromium for tanning purpose instead of hexavalent chromium (carcinogenic). Metal complex dyes, which contain restricted heavy metals and benzidine based dyes must be replaced. The chlorinated fatliquoring agents and retanning products should be replaced with the easily biodegradable products.
Green fleshing of hides	Green fleshing just after deep soaking is a suitable procedure to obtain by-product at pH

	close to neutral, which can then easily be processed to recover fats and proteins with good marketing possibilities and to save liming and unhairing chemicals. Further green fleshing also improves the penetration of the chemicals and hence improves the quality of finished leather.
Hair shaving methods	Hair saving system use smaller quantities of sulfide as compared to hair destruction system, and allows easy separation of the protein constituted by the undissolved hair and hence imply less pollution than the hair dissolving process. The procedure results in a significant reduction of COD, BOD5 , nitrogen, sulfide, total and suspended solids in the wastewater, besides a decrease of sulfide consumption. The hair saving would decrease the organic load for treatment plant.
Recycling Liming Liquor	Some of the liming unhairing techniques permit a direct reuse of the spent liquors after decantation and/or filtration. The procedure permits savings of water, sulfide, and lime.
Recycling of un- hairing liquors	By reuse of un-hairing liquors after separation of insoluble substances by sedimentation important savings are claimed including 50 % sulphide, 40% lime and 60% of process water
Lime Splitting and trimming	Splitting and trimming is usually carried out after tanning which results in a by-product of low quality containing chromium in it. If these operations are carried out with the pelt, the produced by-product can be sold easily in the market than those resulting from splitting and trimming of wet blue (tanned hides/skins). The un-tanned solid waste will be a good raw material for manufacturing of gelatin or animal feed. This will also results in a reduction in the quantities of chemicals used for deliming, pickling, tanning and consequently the load of the pollutants in wastewater will be considerably reduced.
Application of weak acids in deliming process	Application of weak acids (organic) can eliminate the discharge of ammonium salt from deliming process

6.5.1 High Exhaustion

(Blackman A., (2005)) Using special inputs and procedures to ensure that more of the chrome in the tanning bath actually affixes to the hide, and less ends up in waste streams. Although this technique requires a more expensive type of chrome (self- basification) and a longer soaking period, it offers significant cost shavings due to reduced overall use (UNEP 1991)

6.5.2 Enzyme InTthe Dehairing Bath

*S*ubstituting biodegradable enzymes for lime and sodium sulfide.

6.5.3 Recycling The Dehairing Bath

Saving and reusing the contents of the dehairing bath instead of discharging it all into the sewer after a single use. This simple technology requires only fixed investments in a holding tank, a pump, and a filtering system to remove suspended solids (usually a simple wire mesh screen). Because the chemical inputs into the dehairing bath are relatively inexpensive, only minor cost savings accompany the environmental benefits.

6.5.4 Recycling In The Chrome Tanning Bath

Reusing contents of the tanning bath instead of discharging them into the sewer after a single use. Like recycling the dehairing bath, this simple technology requires only fixed investments in a holding tank, a pump, and a simple filter. It can reduce chrome use by up to 20%. (UNEP 1991). [Blackman A., (2005), *Adaption of Clean Leather- Tanning Technologies in Mexico*]

6.5.5 Reuse Of Chrome

Quite a few options are available for the reuse of the chrome discharged in the tanning effluent. These technologies do not completely eliminate the chromium being discharged through the effluent or sludge. However, it can be seen as apart of a general environmental plan of the tannery, since it reduces the necessary amount of chromium being discharged into the environment, thus facilitating the treatment and disposal of small amounts of chromium containing sludge. Chrome reuse option also provides financial benefits.

6.5.6 Direct Recycling Of Chrome Tanning Float

This is the easiest method of chrome reuse. In this method after collection and sufficiently fine screening, the float is controlled and the chromium amounts used in the previous cycle are replaced by fresh chromium salts. Depending on the tanning technology in use, the degree of exhaustion reached for each cycle may vary. The recycling method may be repeated several times on the same float. However, it is limited by the occurrence of quality problems with delicate hides and by the need to control residual float. This technology is suitable for small tanneries.

6.5.7 Recycling Of Chrome After Precipitation

This allows collection of the tanning float with the rinses, that sometimes occur at the end of the tanning and the effluent from various post-tanning stages (washing, dripping, sammying, etc). After collection, screening and storage, the floats are precipitated with different types of alkalis and bases including sodium hydroxide, sodium carbonate, magnesium oxide and even with lime. The reuse of sludge after simple settling and acidification has been experimented and practiced. Schematic diagram of a typical chrome recovery and reuse plant is shown in Figure 6.1. Large plants have operated under this scheme for many years in Germany, Italy, South America and France. [Office for Official Publication of The European Communities,(2003)]

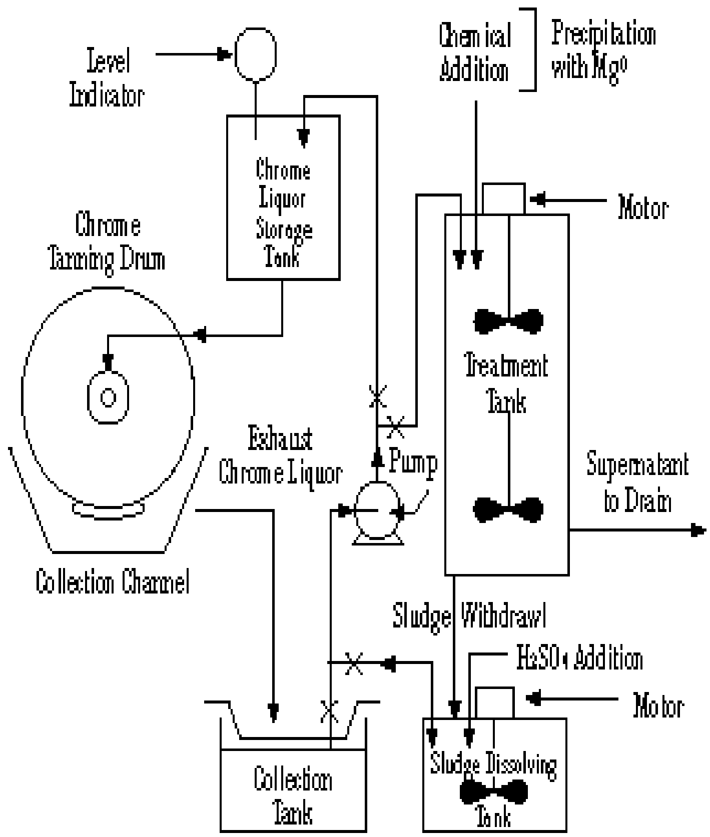


Figure 6.1 Chrome Recovery & Reuse Plant

Tanners in developing countries can reduce the pollution load by pursing low waste technologies. This will, in effect reduce the amount of capital investment that will be required in the treatment of effluent through a reduction in the size of facility needed. By limiting pollutants in the streams, the quantities of effluent treatment chemicals will be commensurately limited. Tanneries should also maximize their returns on residues from sludge and solid waste; investigating the feasibility of extracting methane, saving hair for conversion into felt; turning waste split and untanned trimmings into gelatin; protein powders and collagen for sausage casings and medical and surgical films; turning fleshing into glue, animal feed protein and fertilizers and tanned waste into leatherboard, filter media, non- wovens and other and uses. By commercializing solid waste, the cost of effluent can, to some extent be covered.

Biogas can be recovered by anaerobic digestion of sludge. Biomethanization reduces the volume of sludge and improves its stability and thereby yields a material more acceptable to landfill. However, owing to the presence of some toxic and corrosive components the biogas produces has to be purified before use.

Solid waste can be a useful source of chemicals and protein. For instance it is possible to recover chromium from chrome leather shavings and waste by enzymatic hydrolysis. Leatherboard can be produced from vegetable tanned shaving and trimmings. It is also possible to use chrome tanned waste, although the quality of the leatherboard is not as high.

Untanned trimming have long been a traditional source of gelatin and untanned fleshings, a source of glue. Tallow and grease can be obtained from fleshings by rendering. Perhaps the most interesting developments in recent years have been those that have highligted the possibility of producing protein suitable for animal and fish feeds from solid wastes. They can be used alone or in combination with soya and/ or synthetic amino acids to supplement the deficiencies in collagen.

Flesh splits can be converted into collagen casing. Collagen dispersions can be coagulated with natural and synthetic rubber lattices to give low density rubber shoe soling material. Collagen can be incorporated in coating materials, in pharmaceutical applications, as an absorbent material for filtering sulphur dioxide and other air pollutants. Protein hydrolysates can be applied in the manufacture of cosmetics. They can also revert to the leather industry, being incorporated at the pretanning stage and contributing to the subsequent better uptake of tanning materials. [*Leather Industry,* (1991)]

CHAPTER SEVEN
ENVIRONMENTAL IMPACT OF TANNERY WASTES

Water with a low pH is corrosive to water- carrying systems and in unfavorable circumstances, can lead to the dissolution of heavy metals in the wastewater. The high pH in tannery wastewater is produced by lime because it is used in excess quantities and this causes scaling in sewers. Whereas, low pH of wastewater is caused by use of acids in different tannery processes. A large fluctuation in pH exerts stress on aquatic environment which may kill some sensitive species of plant and animals living there.

Large quantities of proteins and their degraded products form the largest single constituent group in the effluent. They effect the environment which can be expressed by two composite parameters; Biological Oxygen Demand (BOD5) and suspended solids.

BOD is a measure of the oxygen consuming capacity of water containing organic matter. Organic matte by itself does not cause direct harm to aquatic environment, but it exerts an indirect effect there by depressing the dissolved oxygen content of the water. The oxygen content is an essential water quality parameter and its reduction causes stress on the ecosystem. As an extreme example, a total lack of dissolved oxygen as a result of high BOD can kill all natural life in an effected area.

The Chemical Oxygen Demand (COD) is a measure of oxygen equivalent to that portion of the organic matter in a sample which is susceptible to oxidation by a strong chemical oxidant. It is an important, rapidly measured parameter for stream and industrial waste studies and for control of waste treatment plants.

Along with the organic compounds immediately available to the stream organism, it also determines biological compounds that are not a part of immediate biochemical load on the oxygen assets of the receiving water.

Due to sulfide discharged from the unhairing process, hydrogen sulfide is released at a pH value lower than 8.5. This gas has an unpleasant smell even in trace quantities and is highly toxic to many forms of life. In higher concentrations, fish mortality may occur at a sulfide concentration of 10 mg/l. Sulfide in public sewer can pose structural problems due to corrosion by sulphuric acid produced as a result of microbial action. Sewage contains sulfide in the range of 15- 20 mg/l. and composite tannery wastewater contains 290 mg/l.

Suspended solids, apart from being societal nuisance, have their main effect when they settle. The layer so formed on the bottom of the watercourse, covers the natural fauna on which aquatic life depends. This can lead to a localized depletion of oxygen supplies in the bottom waters. A further secondary effect is the reduced light penetration and consequent reduction in photosynthesis due to the increased turbidity of water.

The sodium chloride used in the tannery produces no effect when discharged into estuaries or the sea, but effects fresh water life when its concentration in a stream or lake becomes too high. There is no economically viable way of removing salt from the effluent. A similar problem also exists for sulphate used as the chrome tanning salt. Sulphate in addition causes corrosion to concrete structures.

Finishing chemicals like acetic acid, formaldehyde, ethylene glycol, etc. are used in the tannery processes. The vapors of these chemicals are very dangerous and can affect the health of workers severely. [*The Leather Sector,* (1998)]

CHAPTER EIGHT
MASS BALANCE OF LEATHER PROCESS

This research is taken from J. Buljan, G. Reich, J. Ludvik (*Mass Balance In Leather Processing*, (2000)) The essential part of any tannery waste audit is assessing the efficiency of existing operations carried out during the leather manufacturing process. Typically, tannery staff has a good idea of, and comparatively accurate figures on, the waste resulting from however, do they have a proper overview of the entire range of waste generated. Thus, when considering various cleaner Technologies or waste treatment systems, having access tanner facing arduous choices.

This paper attempts to provide a comprehensive computation of a mass balance and the efficiency of the leather manufacturing process for a tannery, seen as a closed processing bovine hides and producing upper leather for shoes. With minor exceptions (batch washing instead of continuous rinsing, splitting in lime, roller coating), it follows the conventional process. The figures, however, are from various, specific shopfloor data, personnel experience and estimates, as well as from literature. The process formulate are given in Appendix II

Inevitable, given the well- known, wide variations in raw materials, processing methods and equipment used, and the variances in final product spacifications, certain basic assumptions had to be made. These are summarized in the introductory table overleaf. For the sake of simplification, some aspects of the process have been disregarded (energy balance) or not fully elaborated (water balance in drying).

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

The model used in this research shows that only 53 % of corium collagen and 15 % of the chemicals purchased are retained in the finished leather. The challenge over the next decade will be to reduce this profligate waste of resources. Assumption for mass balance of leather processing is shown in Table 8.1 below.

Table 8.1 Assumption for mass balance of leather processing

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

8.1 Beamhouse Work

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

- **Corium:** Collagen containing the true "leather-building substance"

- **Epidermis:** Mainly hair, cells and certain protein-like substances that are removed through liming

- **Subcutis (subcutaneous tissue):** Collagen and certain other proteins including fats, that are removed by fleshing during beamhouse processes **(flesh)**

For the same reason, substances of lesser quantitative importance such as soluble proteins and proteo-glycanes have been disregarded. The typical composition of a wet salted hides is given in Figure 8.1 below.

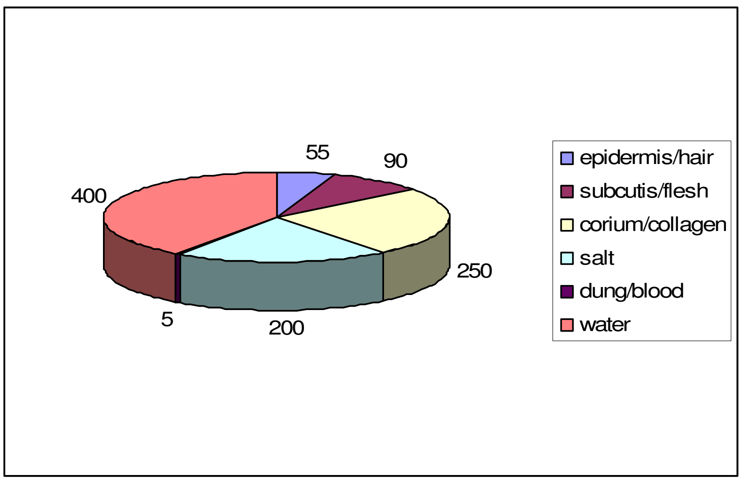


Figure 8.1 Main components of wet salted raw hides in kg/ 1000 kg of wet salted hides

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

For this reason both possibilities have been taken into consideration when illustrating the process flow in the beamhouse is given in Figure 8.2.

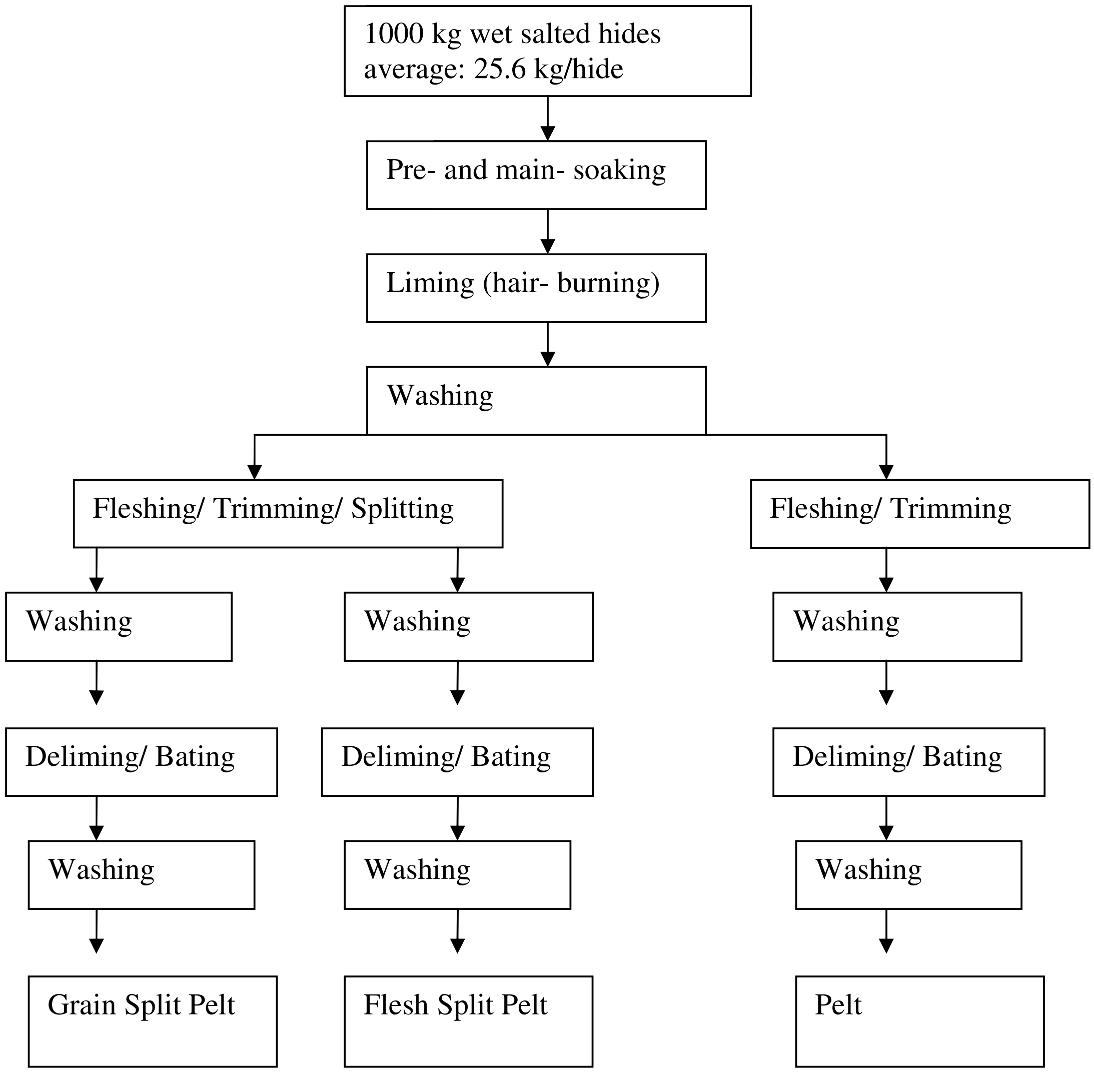


Figure 8.2 Flow diagram of beamhouse operations

Left: splitting after liming *Right: without splitting*

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

Trimming and fleshing take place after liming, although in practice some tannery trim and flesh in green.

Depending on such factors as raw hide characteristics, technology and range of final products, the amount/ weight of unsplit pelts, splits (grain and flesh), trimming and fleshing varies widely. The data is given in Table 8.2 are to be seen as typical average values.

Table 8.2 Mass balance: beamhouse without splitting and splitting after liming

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

The composition of fleshing and trimmings also varies widely. The mass balance in Table 8.3 is based on average values

Table 8.3 Composition of fleshing and trimmings

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

8.2 Chrome Tanning

To all intents and purposes, the pelt, i.e. the raw material entering the tanyards, is virtually only composed of collagen and water; the small amount of fat, salts (e.g. calcium salts) and tensides that remain after beamhouse operations have been disregarded in the computation. The typical composition of a pelt prior to tanning is shown in Figure 8.3.

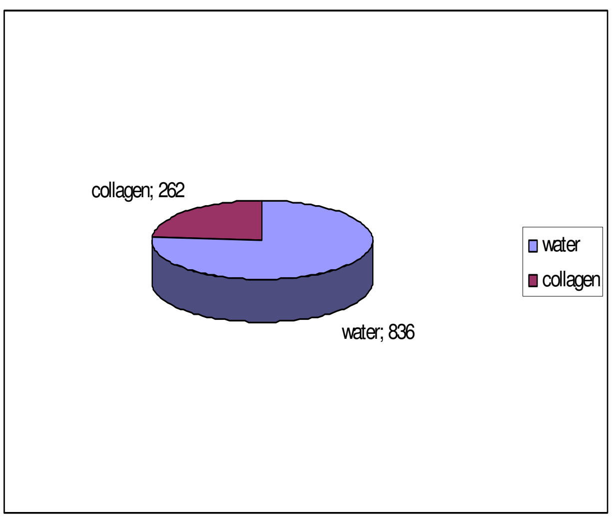


Figure 8.3 Main components of pelt (kg/ 1100 kg pelt weight)

The main steps in a tanyard using conventional technology, i.e. not using any type of recycling, high exhaustion or chrome recovery process, are shown in Figure 8.4.

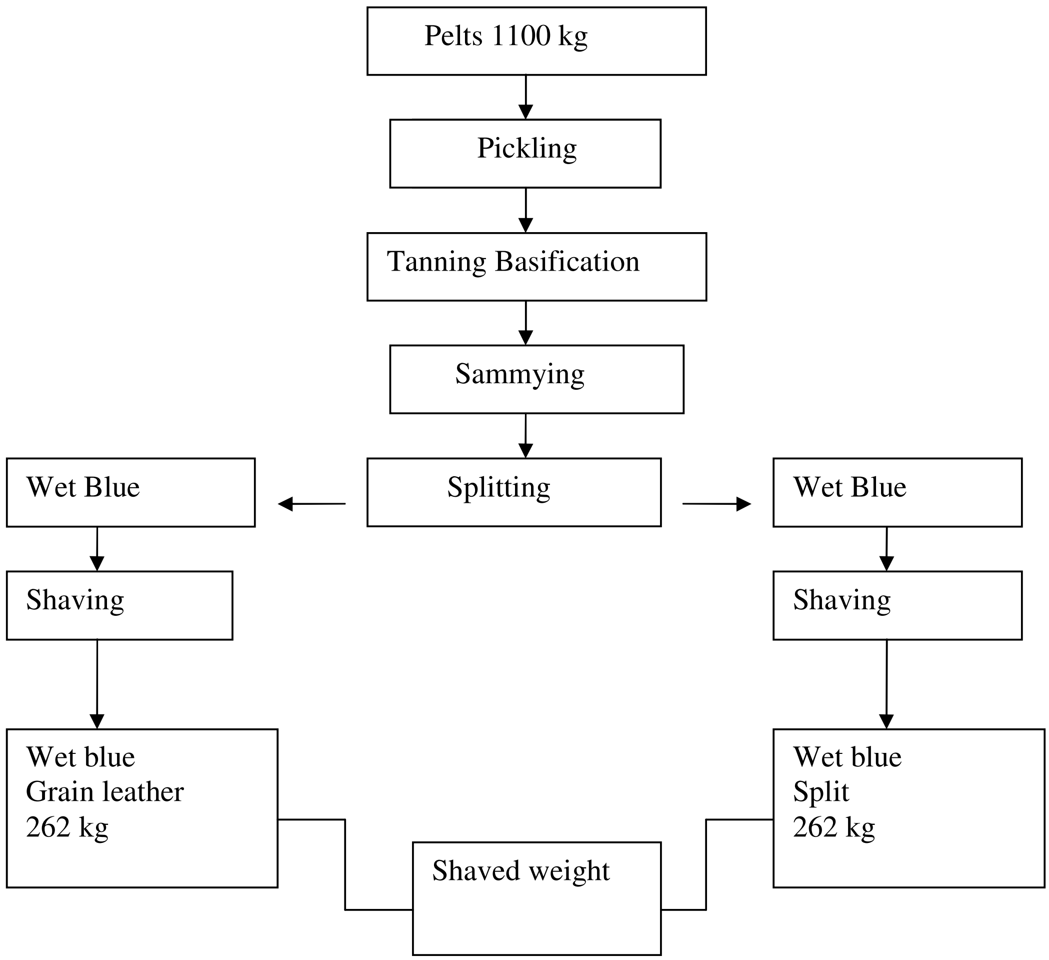


Figure 8.4 Flow diagram of chrome tanning of unsplit pelt

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

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

At the end of chrome tanning, some 75 per cent of the chrome offer (Cr_2O_3)remains in the collagen structure. Small amounts of other chemicals and auxiliaries such as tensides, acids and bases (in the form of soluble 'reaction salt') remain in the wet blue leather. The presence of calcium is very common and occasionally causes irregular dyeing. In terms of weight, all such residues can be disregarded. Mass balance of the tanning processing is shown in Table 8.4.

Calculation Of The Chrome Balance:

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

Exhaustion: About 75%: about 1. 5% Cr_2O_3 reacts with the collagen of the pelt in the form of a bi-nuclear basic chrome sulfate complex.

Cr_2O_3 : $Cr_2(SO_4)(OH)_2$ ratio: 152: 234 (f: Cr_2O_3 x 1. 55)

Table 8.4 Mass balance of the tanning process

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

The primary concern of tanners and environmental protection authorities alike is the chrome balance. A typical distribution for a conventional main tanning process is shown in Table 8.5

Table 8.5 Chrome balance of the main tanning process

Input: % and kg/ 1100 kg limed pelt weight; Output: kg

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

The composition of the resulting wet blue reflects the change the pelt has undergone during the chrome tanning process. Composition of pelt, wet blue grain leather and wet blue split leather is shown in Figure 8.5.

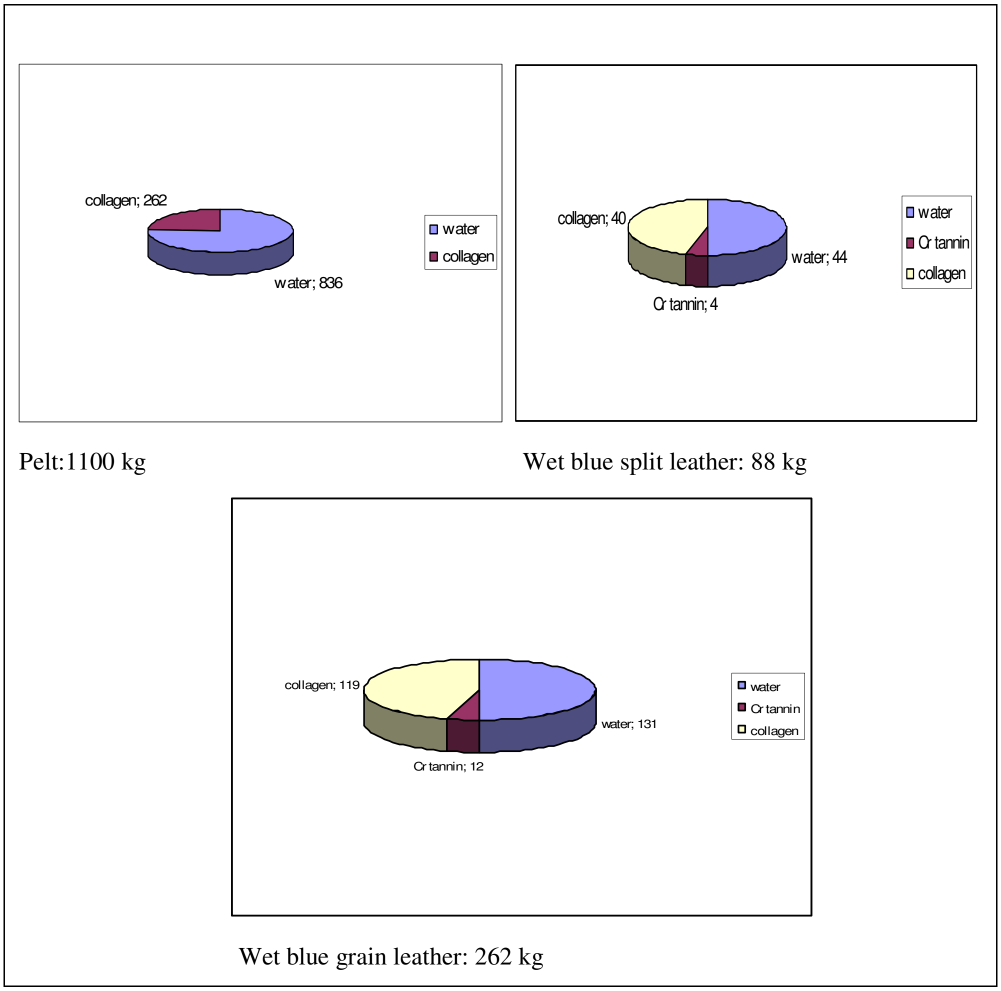


Figure 8.5 Composition of pelt, wet blue grain leather and wet blue split leather
Chrome tannin calculated as bi- nuclear chrome sulphate complex

8.3 Post- Tanning (Wet Work)

At this stage of manufacture, the starting material is wet-blue grain leather and splits, the composition of which was shown in Figure 8.6. The variety of and differences in post-tanning wet work formulations followed by tanners (even when producing very similar types of leather) is much broader than in beamhouse and chrome tanning. Nevertheless, whereas the chemicals used, float length, duration, temperature and sequence may differ, several steps involved in converting wet blue (both grain leather and splits) into crust leather can be considered typical for most tanneries.

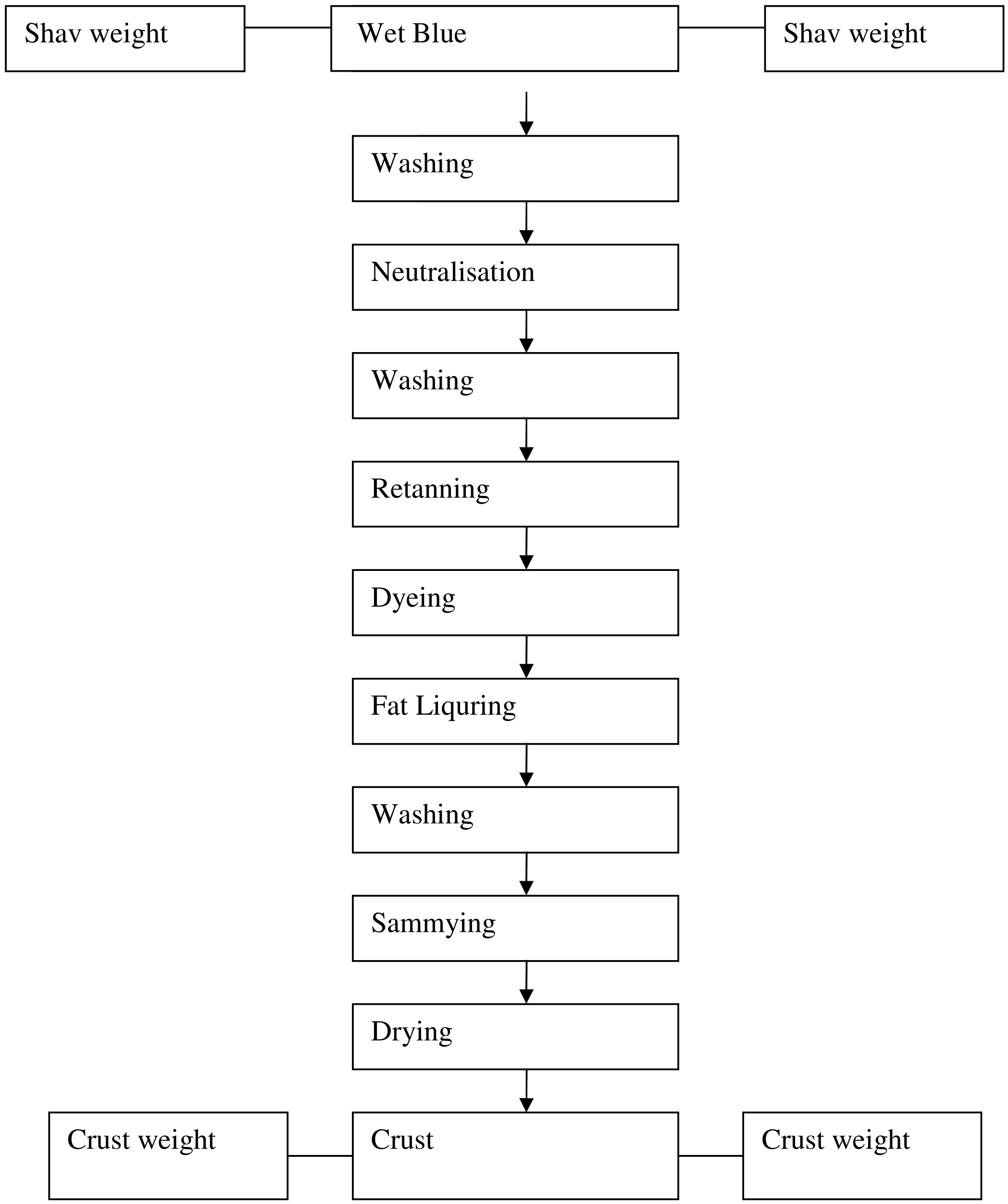


Figure 8.6 Flow diagram for post-tanning wet-blue grain leather and split

The amount of chemicals, i.e. the additional components absorbed and retained by leather in wet finishing, depends primarily on the offer (quality) of a certain chemicals, its active substance content and degree of exhaustion that is shown in Annex II. A typical mass balance for wet-finishing operation is given in Table 8.6 (grain leather) and Table 8.7 (split) . The composition of crust leather reflects the change in wet blue due to post- tanning processes is shown in Figure 8.7.

Table 8.6 Mass balance of post tanning operation – wet blue grain leather

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

Table 8.7 Mass balance of post tanning operation – wet blue split leather

*Only water evaporation taken into account

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

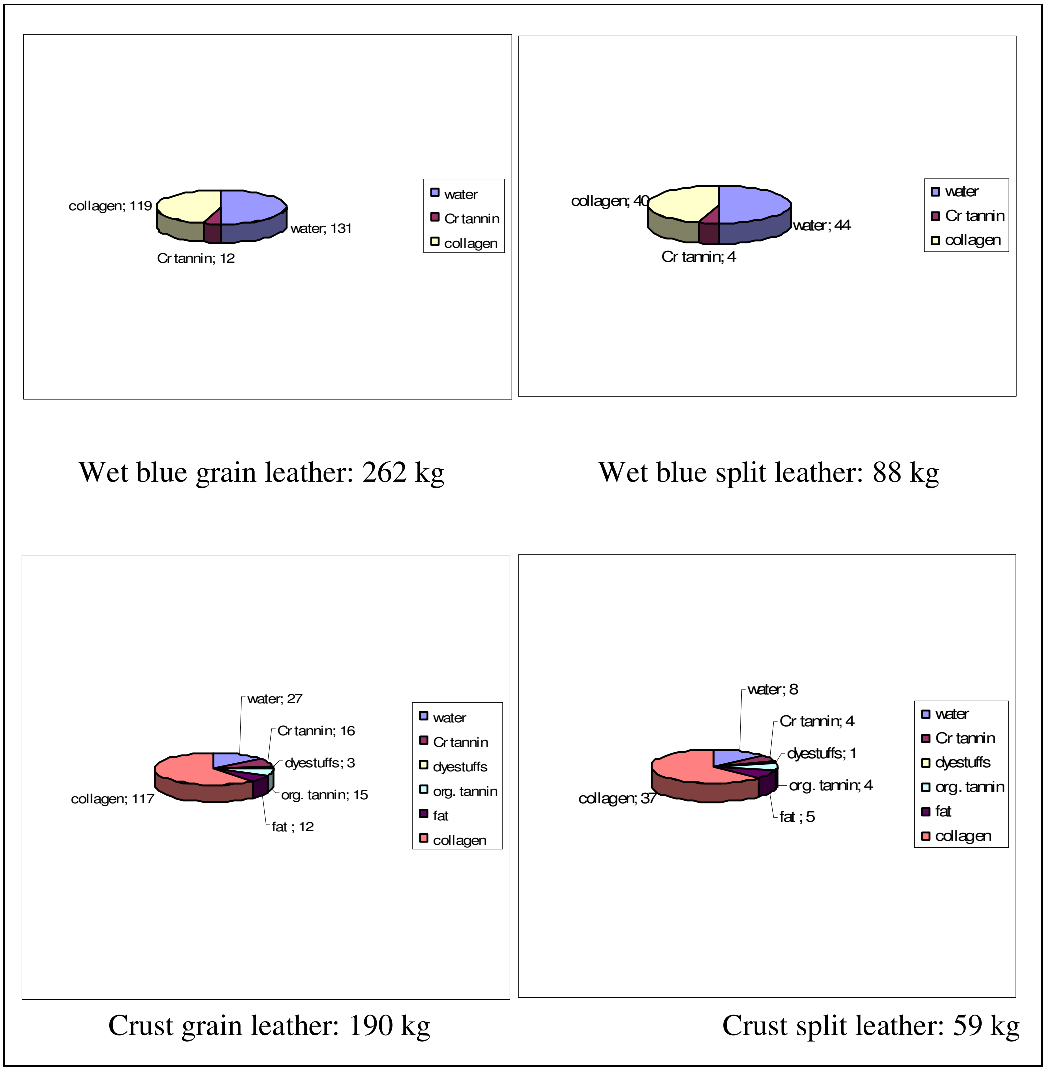


Figure 8.7 Composition of wet blue and crust grain leather (left) and wet blue and crust split leather (right)

8.4 Finishing

It is hardly possible to find two tanneries following exactly the same finishing procedure and, more particularly, the same finishing formulation even when they use the same raw material in order to produce the same type of finished leather. Furthermore, the operational differences in finishing grain leather and splits are considerable. Typical operations in a finishing department are shown in Figure 8.8.

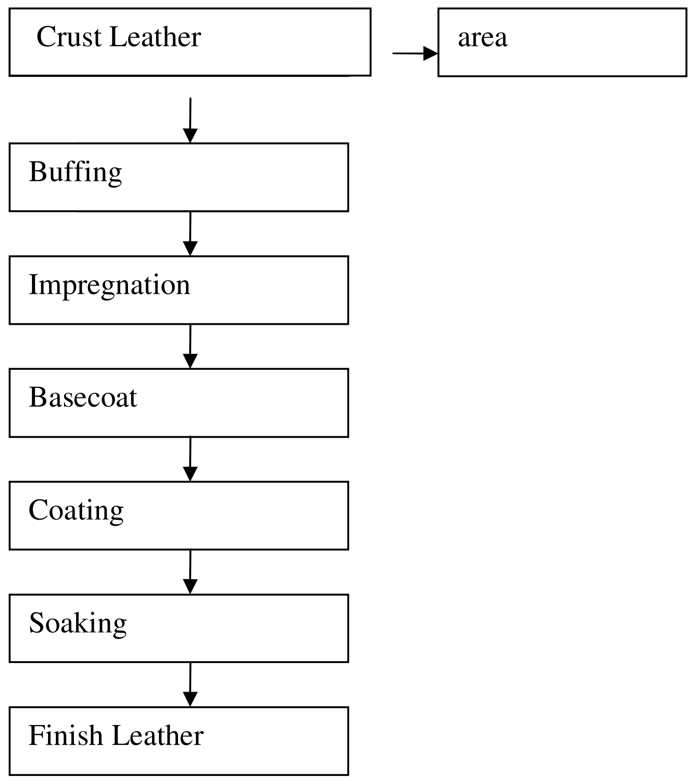


Figure 8.8 Flow diagram of finishing of crust leathers (grain and split)

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

The amount of chemical needed for coating is always calculated according to area: in grams per square meter (g/m^2). Finishing chemicals are normally supplied and subsequently applied in liquid form. The active ingredient component is expressed in terms of dry matter content. The amount required and ultimately applied is determined on that basis. Loss of chemicals, trimming and water consumption were taken into account when calculating the mass balance in finishing is shown in Figures 8.9 and 8.10. [Buljan, J., Ludvik, J., Reich, G., (2000)]

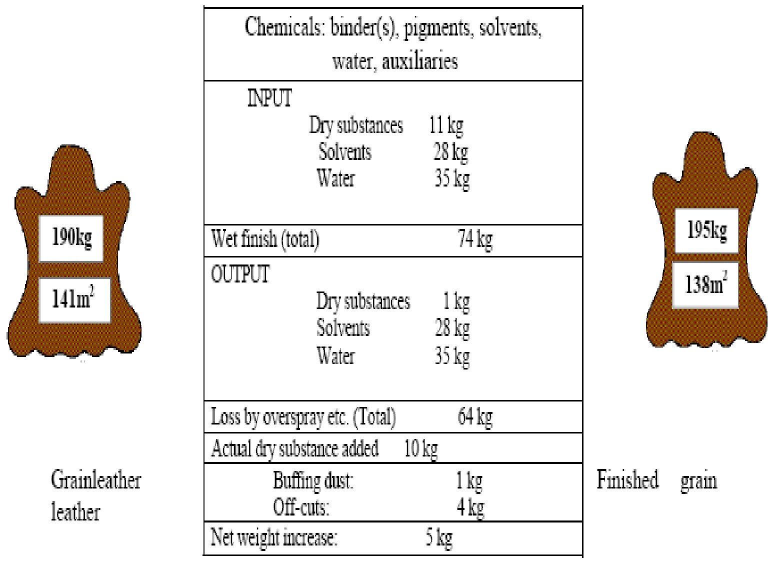
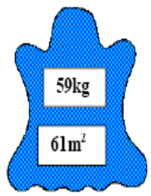
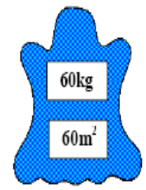


Figure 8.9 Mass balance: Finishing of grain leather
(in kg/ 141 square meter crust grain leather)



Split leather

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



Finished embossed split

Figure 8.10 Mass balance: Finishing of split leather

(in kg/ 61 square meter crust split leather)

CHAPTER NINE
FACILITIES

9.1 Izmir Menemen Leather Free Zone

9.1.1 History of Menemen Leather Free Zone

Due to downtown highway construction and legal expropriation activities carried out by the authorities, and the environmental pollution in the centrum, it was deemed better for the Leather Production Facilities so long located in İzmir-Yeşildere and its surrounding to move out of the city for a new settlement for further economic activity.

Therefore, the leather Industrialists mostly concentrated at the İzmir-Yeşildere region founded Izmir Leather Industrialists' Cooperative Construction Works with 138 partners, each with a limited liability in the year 1984. They commenced activities within a new settlement plan with an aim to increase their contribution in the country's economy.

In line with the decision of the Board of Consultants formed by the authorities of the Governor General of Izmir Province, the present land of the free zone was purchased at a distance of 3. 5 kilometers to the Menemen- Maltepe village, having taken into consideration its convenience for the leather industry. Settlement plans and the joint treatment plant projects as well as drinking and utility water, sewage system, roads and energy distribution projects for the factories followed the purchase.

In the reconstruction plan prepared, land usage was distributed as followed:

911. 038 m² (56. 2 %) as industrial plant areas and secondary industrial areas,
102. 485 m² (6. 3 %) as social and administrative areas
237. 181 m² (14. 6 %) as roads

22. 375 m² (1. 4 %) as parking lots

347. 404 m² (21.5 %) as recreation grounds.

As a result of the joint activities carried out with the Ministry of Industry and trade in the second half of the 1988, our zone was included within the goverment program under the name of the Izmir Organized Leather Industry Zone and an Enterprising Committee was formed, whose members consisted of the from the Office of the Governor of the Izmir Private Administration Directorate, Aegean Region Chamber of Industry and the Cooperative Construction Work.

Contracts for the construction of infrastructure and electricity establishment were signed on 18.12.1988 and in 1990 respectively and both were completed by 31.12.1991. Construction of the wastewater treatment plant was started on the 01.12.1991 and upon its completion by 1993, the zone started to operate after Mr. President Suleyman DEMIREL made its inauguration. The zone is made of 189 parcels, hosts 247 companies with activity licenses. 3222 people were employed in the zone in100 active companies with the figures of year- end 2004. While its sale capacity was 500 million $ in 1997, its trade volume increase up to 309.160.857, 27 $ 2004, after it was transformed into a free zone.

9.1.2 Present Situation of Menemen Leather Free Zone

Menemen Leather Free Zone is dominant on the leather markets of EU (European Union) countries, Russia and Middle East and it is the industrial center, which is a leather in the procurement and treatment of raw leather. Izmir Menemen Leather Free Zone, which is the right address for leather processing and production, offers parcels with established infrastructure and factory premises ready for use especially for secondary industries of the leather sector and all heavy metal industry.

Trade companies can rent close- open spaces for storage purposes. In addition, decree of General Directorate of Customs, under Prime Ministry Under

Secretariat of Customs, (dated 21.02.2004 and numbered 2004/ 2) foresees the performance of the entry transactions of goods without EU origin to the free movement, from our zone.

All companies engaged in investment/ production or commercial activities have to obtain activity license from General Directorate of Free Zone State Under Secretariat of Trade, in order to work in Izmir Menemen Leather Free Zone. Distrubution of area in Menemen Leather Free Zone is given in Figure 9.1. [*Izmir- Menemen Free Zone,* (n.d.)]

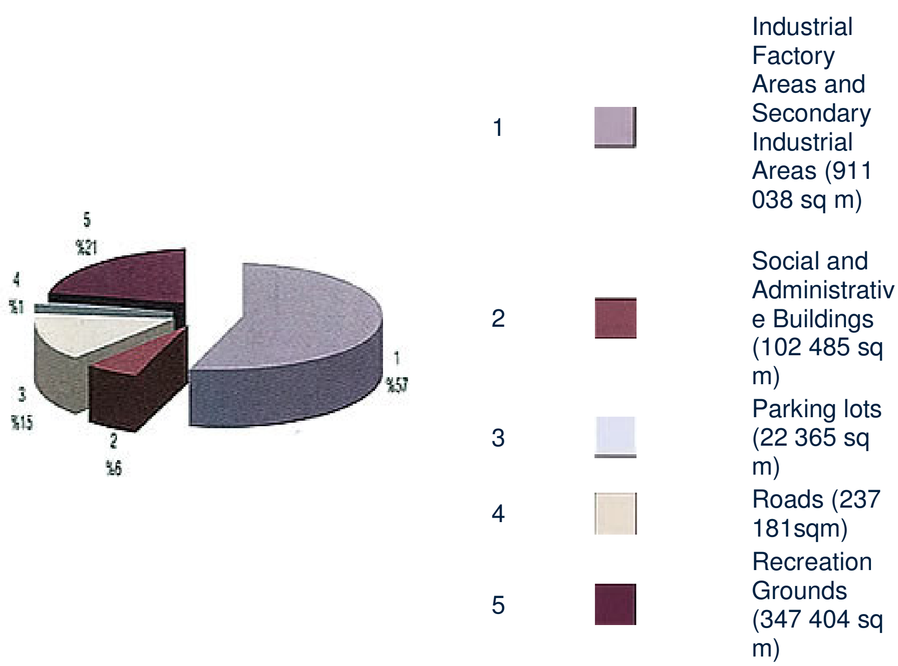


Figure 9.1 Distribution of area in Menemen leather free zone

9.2 Company A

The company A was founded in 1967 and began production as Hamza Sevimli Leather Industry in Izmir Menemen Leather Free Zone. First years, it started production with catttle leather then started production of goat leather shoes and is stil continues. The firm has been running by Hamza Sevimli' s son Eyup Sevimli since 1985. First plant managements according to the Regulation on Water

Pollution Control in Turkey. This regulation is shown in Appendix I. (*Su Kirliligi Kontrolu Yonetmeligi, (2004))*

- Area of Company A: 6212 m²
- Number of Workers: 79
- Energy Consumption: 808. 326 Kwh/ 10 months

9.2.1 Wastes Treatment of Company A

The water getting out of Company A is sent to the plant the pre-recovery is followed, through three different channels differentiate according to their characteristics.

These channels, in accordance with the characteristics of the waste water are;

1. The waste water upgraded from the channel to the plant is coming out of these units below.
   - Soaking
   - Unhairing and liming
2. The waste water upgraded from the channel to the plant is coming out of these units below.
   - Deliming
   - Degreasing and Batting
   - Pickling
   - Tanning
   - Basification
3. The waste water upgraded from the channel to the plant is coming out of these units below.
   - Sammying
   - Retainage
   - Dyeing
   - Fixation

The measured parameters of the waste water are given for their characteristics in the Table 9.1and the Table 9.2.

There are two wastes that are originated both liquid and solid. Account of these wastes;

Liquid Wastes;

Table 9.1 Amount of liquid wastes in Company A

Plants of Factory	Household Wastes(m^3/ d)	Wastes(m^3/ d)
First Plant	50	1664
Second Plant	353	2990
TOTAL	**403**	**4654**

Solid Wastes;

Table 9.2 Amount of solid wastes in Company A

Leather Process	Amount of Wastes (kg/ d)
Tanning	130
Shaving	200
Packing	120 (4- 5 boxes)
Fleshing	120
Trimming	300
TOTAL	**1230**

9.3 Company B

9.3.1 History of Company B

It had been incorporated under the title of " Mehmet SEPICI Skin Dyehouse" at Basma section of Izmir in 1930, when was not even an industry in Turkey. The company was moved to its new tanneries in 1974, located on 40 thousand m² area at Torbali. Company B is serving the world market with ISO 9000: 2000 quality Certificate and with specially equipped laboratories. In this tannery complex, the raw materials or skin and hides are processed to shoe, upper, lining, bag, belt and upholstery leathers.

9.3.2 Environment

Company B has been continuing its activities since 1974 Caybası district in Torbalı town is an organization dealing with the production of lining, stout leather and upper for shoe industry. After the establishment of refinery in 1989, it is till then continuing activities and also a Discharge Permission Document has taken from the public organizations.

Employee from the Directorate of Province of Environment control permanently obedience to discharge rules. Also there is a Group B Emission Permission Document given for convenience for the quality of air and a First Class Opening License for Unhealthy Enterprises which is given for convenience for the health of public and environment.

VOC filtered chimneys suitable for ecology in finish machines for preventing the dust which has come to existence because of leather sandpapering and the equipments for the obstruction of the dust in sandpapering units are the other indications of Company B's sensitivity to the environment.

Within all of these efforts, studies on reducing and evaluation of churns coming out of production has been continued for the reduction of the air pollution in the environment and at last realized “Lime Fleshing Processing Plant “ which has been found valuable for support by STRCT (Scientific and Technical Research Council of Turkey) and TDFT (Technology Development Foundation of Turkey). Company B’s firm has got rid of churn problem and also gained financial gain of protein and fat by foundation of this plant.

Company B’s firm has got rid of churn problem and also gained financial gain of protein and fat by foundation of this plant. Company B’ s firm is following the technological development dealing with environmental carefully and continuing the investments related to this subject. [*Sepiciler*, (n.d.)]

9.3.3 Company B Waste Treatment

Company B’s firm firstly initiated the activities to establish a waste recovery plant for treatment of the waste water. Company B’s facility, operating since August 1989 without any interruption, consists of mechanical, chemical and biological recovery units which have daily 1000m^3 for waste water recovery capacity.

To decrease the pollution mass coming through the recovery plant, the waters coming from the deliming stock are passed through hair binding equipments before being released to the channels.

The waste water is gathered through two different channel systems in the factory and transferred to the waste water treatment plant through two other different channels. Without mixing chromium wastewater and lime waste water with each other, they pass through coarse screening, grit chamber and micro screens in sequence. The waste water passed through chromium micro screening is taken to the equalization basin, the waste water passed through lime micro screenings is taken to the sulfur oxidation ponds. The waters purified from sulfur in sulfur oxidation pond flow to equilibration pond by the help of an inundation canal. The waste water reaching enough homogeneity and airing is taken to chemical recovery unit. Here, by the help of the chemicals has been added, the materials which can be purified through chemical recovery through overbearing techniques and banished from the water. The materials banished from water called as treatment sludge is sent to the sludge dewatering unit. The waste water is sent to the biological treatment unit. The biological system is an extended aeration system, where through bacterial activity named activated sludge both carbon and nitrogen treatment is accomplished. The water passing to the clarification unit after a sufficient waiting period is disposed to recipient environment through the channels. The active sludge is recycled back to the biological treatment unit. The treatment sludge in the clarifier is dewatered by means of belt-press and made ready and sent for disposal. Discharge standards and diagram of wastewater treatment plant of second plant are shown Figure 9.1 and Table 9.4 below:

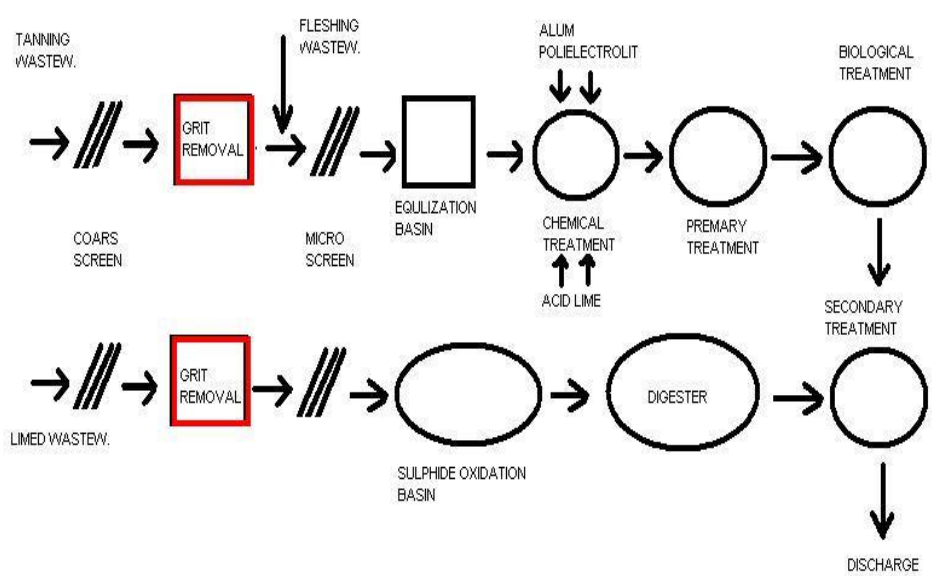


Figure 9.1 Wastewater Treatment Plant in Company B

Table 9.4 The discharged standarts of Company B

Unit	Amount
COD (mg/l)	168
SS (mg/l)	47
TKN (mg/l)	75
Oil/ Grease (mg/l)	6. 8
Sulphade (mg/l)	< 0. 1
Total Chrome (mg/l)	0. 2
pH	7.76

9.4 Comparison

The general information about Company A operating in Menemen Free Leather Zone and Company B operating in Torbalı, İzmir is given in the Table 9.5 below:

Tablo 9.5 General information about Company A and Company B

Characteristics	Torbalı/Company B	Menemen/Company A
The field allocated for production (m²)	17000	11000
Storage and stocking Field(m²)	3000	1500
Green and empty field	40000	3500
Total field(m²)	60000	16000
Restaurant Capacity (person)	250	150
Cafeteria Capacity(person)	-	150
Number of workers	70	77
Number of Administrative personnel	22	
Number of Technical personnel	16	
Number of shift	1	
Working period	(8:00-18:00)	(8:00-18:30)
Operation period of the facility	240/5	300/5

In addition to these information; the waste water of Company B is processed through treatment, is disposed to the sewer system after appropriate standards are met. Wastewater of Menemen Free Leather Zone is collected by 3 different channels, on condition that pre- treatment process is completed in a plant where all pre-treatment facilities of the undertakings of the zone has been carried out and the waste water is disposed to the sewer system.

The trim waste of Company B is used in various industrial branches as a raw material. The trim waste of Company A is also used in supplier industries as a raw material. However, unfortunately shaving waste can not be used today for such reasons as transportation, the distance between the industries etc. whereas in the past it is very useful raw material resource which can be used in various industrial branches.

- Salting is applied in both facilities in order to protect the tanned leathers until they arrive at the facility.

- Both sheep and goat leather and cattle leather is tanned in the second facility while, in the first facility, only sheep and goat leather is tanned.

- While waste products from snipping and trimming processes are not used as raw materials for another industry in the first facility, they are sold as raw materials in the second facility.

- In both facilities, dissolving with lime method is used for hair-removing process, so it is not possible to recycle the hair and in addition, the water is polluted more by the chemicals and leather leftovers. Especially COD and BOD loads are increased more in the water.

- In both facilities, chrome tanning method is used. This method is the optimum method in terms of the characteristics that the leather gains. In addition, elevation and treatment processes are applied, which is different form other kinds of water.

- In the first facility, no treatment process is applied in the activity area, considering the characteristics of the process water in the facility, this water is discharged to sewer system after being elevated to the pre-treatment facility through three separate canals.

- In the second facility, there is a pre-treatment facility in the activity area.

- In both facilities, discharge to the sewer system is carried out in accordance with the Regulations for the Control of Water Pollution published in the Official Gazette No 25687 dated 31 December 2004. Discharging limits between Companies and Limit of Regulation in Turkey is given Table 9.6.

- In terms of the parameters for discharge to receptive environment stated in the Regulations for the Control of Water Pollution, it is observed that the output parameters are in accordance with the Regulations when the two facilities are compared.

Table 9.6 Discharging limits between Compaines and Limit of Regulation in Turkey

Parameters (mg/l)	Company A	Company B	Regulation of Turkey	
			Composite Sample For 2 hours	Composite Sample For 24 hours
COD	~ 250	168	300	200
SSM		47	125	-
TKN	5- 10	7.5	20	.15
Oil/Grease	30- 1	6.8	30	20
S	0.002	< 0.1	2	1
Total Chrome	0. 22- 0. 25	0.2	3	2
pH	7. 7	7. 76	6- 9	6- 9

CHAPTER TEN
CONCLUSION

Nowadays, through advanced technologies, recycling of the chemicals which are necessary in the facility itself and will be burden for the environment, and the recovery of which is costly, is the path should be taken. Although the initial investment cost is considerably high, in the long run the benefits will recover the initial investment cost and minimize the harmful environmental effects. A lot of best available treatment (BAT) technologies is used in leather facilities as (bio) membrane, precipitation process to removal of chromium. Basic principle of these technologies is depended on recovery of chromium in tannery wastewater. The recovery of the chromium of tannery wastewater is necessary for environmental protection and economic reason. Some solid wastes of leather facilities should be use the other sector as raw material. Therefore, the raw material consumption is lower that use of these waste is used the raw material a lot of sectors.

There are many salting methods today (drying, keeping in a temperature of -3 Celsius degree or putting in the ice bars). Even though keeping with salt method is applied since it is economically favorable, it causes an additional treatment cost to the facility. This salt can be detracted from the facility by whipping-by-hand method to a minimum degree. In addition, the slaughter houses are near the leather tanning facilities but this does not necessitate that the leathers should be immediately tanned or additional chemicals or technologies should be used. Since this factor is not considered during the foundation of the facilities, this alternative cannot be used in the process of decreasing the salt added into water.

In the first facility, waste products from snipping and trimming processes were used as raw material in other industries, but in time, these waste products caused additional pollution since the shipping expenses became costly because of the distance between the facilities. In the other facility, these waste products are sold. Waste products from fleshing process are used as raw material in neither facility.

Today the most easily applied method for hair-removing process is using chemicals such as lime, sodium sulfide and kaolin in liming closets, which does not require additional work force. But this method is one of the reasons for the increase of the pollution in the water. Another method is whitening method. In this method, a solution composed of sodium sulfide, lime, supplied hydrate and kaolin is applied on the sub-section of the leather, and the leather is left for 3 hours, then the hair is removed manually. This whitening method should not be ignored since in this method the process water is used and the chemicals and the pollution in the water are kept at a minimum level, in addition, it can be sold and most importantly this method helps energy saving.

Considering the physical characteristics of the leather achieved by the chrome tanning method, this method is used in both facilities for producing desirable quality leather. Vegetative tanning or alternative tanning methods can be used instead of this method. Even though we cannot completely eliminate the pollution that is caused by chrome tanning method, we can recycle chrome by making use of clean technologies to minimize it keeping the pollution of the environment and costs of the chemicals used at a minimum level. The process of minimizing the pollution by recycling chrome is applicable in both facilities without any area problem. This technology is perfect for the big or medium-seized facilities. But it is a fact that, considering the additional processes in the future and unplanned construction costs; the modification of the clean technologies should be subtracted.

Since the first facility is located in a free leather trade area, it is not required to construct a pre-treatment facility because there is a single treatment facility in this free trade area to minimize the wastes from all of the facilities in this area. But wastes from liming and tanning are elevated to the facility in separate canals together with the process water and discharged in accordance with the rules stated in the Regulations.

In both facilities, for the control of the pollution, the most appropriate technologies can be preferred in both refining and operating processes by employing mass balance calculations, which is an additional indicator to the Regulations. The second facility has concentrated on this kind of an activity and is trying to get data for calculations.

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APPENDICES

APPENDIX I

Regulation on Water Pollution Control

Issued in the Official Gazette dated 31st December 2004, Friday No : 25687

First Chapter

Purpose, Scope, Legal Basis and Descriptions

Purpose and Scope

Article 1 — Purpose of this regulation is to determine necessary legal and technical essentials needed to realize prevention of water pollution compatible with sustainable development targets in order to provide protection of surface and underground water sources of the country and to provide usage of them in the best way.

This regulation covers essentials regarding to quality classification and using purposes of water environments, planning essentials and prohibitions regarding to protection of water quality, fundamentals of wastewater emptying and emptying permissions, essentials regarding to wastewater infrastructure facilities and surveillance and audit methods and essentials to be performed in order to provide water pollution.

Legal Basis

Article 2 — This regulation have been prepared on the basis of articles 8 and 11 of Environment Law dated 9/8/1983 and no 2827 and article 9 of Law on Organization and Duties of Ministry of Environment and Forests dated 1/5/2003 and no 4856.

Definitions

Article 3 — In this regulation definitions are as follows:

Ministry: Ministry of Environment and Forests, Receiving water environment: Near or far environments such as lake, stream, shore and sea and underground waters where wastewaters discharged or indirectly mixed in,

Waste: Waste energy with solid, liquid and gas matters effecting usage potentials of the environment and causing direct or indirect damages at the end of any production and consumption activities with their physical, chemical and bacteriological properties by changing composition and characteristics of receiving environments where they mixed in,

Wastewater: Waters those properties have been changed partially or completely or got dirty as a result of domestic, industrial, agricultural and other usages and waters sourcing from mines and ore facilities and waters coming as surface or underground waters as a result of precipitations from city areas such as streets, parking lots and similar places in coated or uncoated city regions.

Wastewater treatment: One or more of the physical, chemical and biological treatment processes performed to provide wastewater regain some or all of their physical, chemical and bacteriological characteristics lost as a result of various usages and/or to prevent those waters to change the receiving environment's physical, chemical, bacteriological and ecological features.

Wastewater sources: Dwellings, commercial buildings, industrial establishments, mines, ore washing and enrichment facilities, urban areas, agricultural areas, industrial zones, repair shops, workshops, hospitals and similar institutions, establishments and enterprises and areas. And those;

a) Important contaminating wastewater sources are industrial wastewater sources refer to more than 1% of the contaminating load or industrial wastewaters with flow rate of more than 50 m3 and total flow of the sewerage system carried in that basin, considering wastewater flow or any of the appropriate pollution parameters (kg/day) including dangerous and harmful wastes.

b) Small wastewater sources are wastewater sources those do not have important contaminating characteristics considering any contamination parameters and load with flow rate less than 50m3/day.

Fish bio-experiment: Used to determine toxic effects of wastewaters on fishes used as indicators organism, a standard experiment providing statement of toxicity in relation with dilution ratios determining percentages of staying alive at the end of 48, 72 and 96 hours in various wastewater dilutions.

Industrial wastewater: Wastewaters remaining from any kind of process and wash sourcing from industrial establishments, factories, workshops, repair-shops, small industrial sites and industrial zones, furnace and cooling waters fend off after processing without mixing with process waters.

Fecal wastes: Urine, faces and remnants of human or warm blooded animals causing contamination of any water masses especially bacteriologically.

Administration: Administration mentioned in the regulation,

Organic waste: Organic matters causing oxygen consumption by decomposing biochemically in mediums they mixed in.

Pre-treatment facilities are: Due to characteristics of wastewaters;

a) To provide acceptance limits into this system for wastewaters gathered by the help of sewerage system

b) To match foreseen limit values for inlet waters of those establishment to accept wastewater treatment and elimination facility of private, common, industrial zone or public by any of the wastewater transporting means.

Industrial Zone: Organized industrial zones active in certain manufacturing fields; tradesman and craftsman sites, fields where small industry zones and establishments with judicial personality making production as cooperatives eliminate their wastewaters with a common system,

Dilution: Magnitude calculated according to characteristics of receiving environment and discharging method of waste water and decrease as a result of various physical, chemical and biochemical reactions or physical, hydrodynamic events in receiving environment as a result of discharge of contamination parameter’s concentration in wastewater in wastewater discharged in a receiving environment

Water pollution: discharge of matter or energy wastes those will cause deterioration in biological sources, human health, fishing, water quality and will prevent use of water with other purposes directly or indirectly and observed as negative change in chemical, physical, bacteriological, radioactive and ecological characteristics of water source

Water pollution control standards: To provide audit according to present quality criteria of water masses planned to be used with certain purposes and limitation values to prevent quality loss and from those limitations;

a) receiving environment standards, stated to prevent obstruction of deterioration of water mass’ quality characteristics deemed as receiving environment because of water discharge.

b) Discharge standards restrained quality characteristics of discharged wastewaters with the same purposes

Dangerous and harmful matters: Matters, causing respiration, digestion or skin absorption and acute toxicity and long-term chronic toxicity, with cancer causing, resistant to biological treatment, necessitating special and elimination process according to Regulation on Water Pollution Control Dangerous and Harmful Matters in Water Notification in order to prevent them contaminate underground and surface waters,

Toxicity: any matter described as toxic threatening human health, health of various indicator organisms ecosystem balance by being in any water environment more than a certain concentration; characteristics of causing any acute or chronic diseases, teratogenic, genetic deterioration and death.

TDF (toxicity dilution factor): A unit used identifying toxicity grade of wastewaters,

CHAPTER TWO

Principles

Principles on protection of waters

Article 4 — For preventing protection and pollution of waters;

a) To prepare permission letters for every kind of polluting sources for control of water pollution,

b) To equalize amount of clean water taken and the amount of wastewater for domestic wastewaters,

c) Determination of most concentrated regions of water pollution in the frame of water quality criteria that will provide classification according to various purposes of surface waters, underground waters and sea water, to make works on most appropriate use of water sources and designation of precedence of precautions those will be taken,

d) Production with technology that will prevent pollution at its source by minimizing waste concentration and wastewater amount.

e) Choosing appropriate technical and economical treatment methods in wastewater treatment,

f) Building common wastewater treatment facility for industries and settlements producing similar wastewaters

g) Design of wastewater treatment facilities as to be make nitrogen and phosphor elimination when needed, where discharge will be made to sensitive areas such as lake, pond, bay, gulf with risk of eutrophication.

h) To take necessary precautions to protect water products production areas,

ı) No receiving environment standard have been submitted in the standard lists for private environment protection regions of which descriptions are made under this regulation; complying with quality parameters of highest quality waters and taking special precautions being separately for each of the groups under water environments quality classification lists given under regulation, Polluting effects of which waters will be protected from

Article 6 — Main effects causing pollution due to domestic, industrial, agricultural wastewaters and sea traffic and similar sources are given below.

a) Fecal wastes,

b) Organic wastes,

c) Chemical wastes,

d) Excessive discharge of nutrition materials causing excessive production to damage the balance of receiving environment

e) Waste heat,

f) Radioactive waste,

g) Materials scraped from the bottom of sea, mud, rubbish and excavation wastes and discharge of similar wastes,

h) Petrol derived solid and liquid wastes from ships and other sea vehicles (bilge water, dirty ballast, sludge, slop, oil and similar wastes),

ı) Other than the abovementioned matters with limit values in Dangerous and Harmful Matters Notification.

Chapter Three

Classification of Water Environment

Industrial Wastewater Discharge Standards

Article 31 — Industries have been grouped according to their production types and sixteen sectors have been formed. Wastewater standards in Table 5-20 aren't applied for the ones completely working in dry type under those sectors. Sectors and industry types of those sectors are given below.

a) Food industry sector: flour factories, macaroni factories, yeast industry, milk and dairy products, obtaining fat from fatty seed and oil refining, olive oil and soup production, solid oil refining, slaughterhouses and integrated meat facilities, fish and bone flour production, slaughter by-products processing, vegetable and fruit washing and processing, plant processing, sugar industry, salt processing, field fishery, water products evaluation and similar industrial establishments.

b) Beverage industry sector; non-alcoholic beverages (soft drinks) industry, alcohol and alcoholic drinks industry, beer and malt production, molasses alcohol production.

c) Mining industry sector; iron and metal ores out of iron, coal production and transport, boron ore, ceramic and earth industry, cement, stone breaking, earth industry and similar by-industry establishments.

d) Glass industry sector; glass goods, flat glass and window glass production, preparing glass wool, silver coated and uncoated mirror production.

e) Coal processing and energy production sector; bituminous coal and lignite coal, coke and town gas production, thermal plants, nuclear plants, geothermal plants, cooling water and similar, industrial cooling waters working in closed circuit, steam boilers working with fuel-oil and coals and similar facilities.

f) Textile industry sector; open fiber, thread production and conditioning, tissue fabric conditioning, cotton textile and similar, cotton gin industry, wool washing, conditioning, weaving and similar, knit fabric conditioning and similar, carpet conditioning and similar, synthetic textile conditioning and similar.

g) Petrol industry sector; petrol refinery, petrol filling facilities and similare.

h) Leather and leather products industry.

ı) Cellulose, paper, cardboard industry sector; half cellulose production, unbleached cellulose production, bleached cellulose production, pure cellulose production, paper production without starch additive, paper production with starch additive, very thin tissue paper production from pure cellulose, surface coated – paper with filling production, production of paper with low percentage of clipping paper, paper production from clipping paper, parchment paper production and similar.

j) Chemistry industry sector; chlorine alkali industry, perborate and other boron products industry; yellow arsenic production and similar, dye and ink industry; dye raw material and auxiliary materials industry; medicine industry; fertilizer industry; plastics industry; pipe, film, hose, rubber industry;

vehicle tyre and rubber coating, medical and agricultural chemicals industry (laboratory, tannin materials, cosmetics); detergent industry; petrochemical and hydrocarbon production facilities; soda production, carbide production, barium compounds production, disperse oxides production and similars.

k) Metal industry sector; iron steel processing plants, in general metal preparing and process, galvanizing, cauterization, electrolytic coating, metal colorizing, zinc coating, watering-hardening, conductor plate production, accumulator production, enameling, glazing, metal grinding and emerying plants, metal polishing and varnishing plants, lacquering-dying, metal production other than iron, aluminum oxide and aluminum melting, iron and other than iron foundries and metal shaping and similar.

l) Wooden products and furniture industry sector; timber and woodwork, chipboard, box, packaging, hardboard and similar.

m) Bulk machine production, electricity machines and equipment, spare part industry sector.

n) Vehicle factories and repair-shop industry; motorized and motorless vehicle repair shops, factories manufacturing automobile, truck, tractor, minibus, bicycle, motorcycle and similar vehicles, shipyards and ship disassembling facilities.

o) Miscellaneous industries; large and small industrial zones and othe industries those sectors couldn’t been determined,

p) Plants producing industrial wastewaters; re-washing waters of drinking water filters, filter water and mud used for air pollution control, gas station, ground and vehicle washing wastewaters, wastewaters coming from solid waste assessment and elimination facilities, wastewaters coming from gas stations, glue and gum production wastewaters, water softening, demineralization and regeneration, active carbon washing and regeneration facilities

Wastewater discharging standards determined for the industrial wastewater sources given above have been arranged from Table 5 to Table 20. Practices for industry types those aren’t covered in this regulation are subject to conformance of Ministry after determinations on discharge standards by relevant administration taking process type of enterprise, used raw materials, chemicals and similar issues into consideration and taking discharge parameters and similar sectors for those parameters and Table 19 as principle.

Pre-treatment Plants

Article 48 — Industries those wastewater infrastructure plants, direct connections to wastewater infrastructure plant don't comply with rules according to administrations due to characteristics of wastewaters are obliged to establish and operate a pre-treatment plant defined under this regulation establishment, operation, maintenance, control and documentation expenses being covered by them.

In addition those concerned are obliged to build and to operate a private treatment plant in the frame of principles defined under article 11 of the Law no 2872 and of which technical feature indicated in connection quality control permission certificate, in the industrial wastewater sources where contamination load is higher than 10% of contamination loads and total flow rate of that sewerage network, according to each parameter given in group standards between Table 5- Table 20 the relevant industrial sector or wastewater flow rate in basin of any wastewater collection basin. In this situation receiving water environment discharge principles and wastewater standards are valid and furthermore owner of the immovable property gets permission from the relevant administration according to article 37 of this regulation.

Table1.Discharge Standards of Leather, Leather Products and similar industries

PARAMETER	UNIT	COMPOSITE SAMPLE FOR 2 HOURS	COMPOSITE SAMPLE FOR 24 HOURS
CHEMICAL OXYGEN DEMAND (COD)	(mg/L)	300	200
SUSPENDED SOLID MATTER (SSM)	(mg/L)	125	-
TOTAL KJELDAHL-NITROGEN	(mg/L)	20	.15
OIL AND GREASE	(mg/L)	30	20
SULFIDE(S^{-2})	(mg/L)	2	1
CHROME (Cr^{+6})	(mg/L)	0.5	0.3
TOTAL CHROME	(mg/L)	3	2
FISH BIO-EXPERIMENT (ZSF)	-	4	4
pH	-	6-9	6-9

APPENDIX II

BEAMHOUSE			
Basis: salts weight, 1000 kg.			
Presoaking	150%	H_2O	1. 5 m^3
	0.15%	Tenside	1. 5 kg.
Main Soaking	150%	H_2O	1. 5 m^3
	0.15%	tenside	1. 5 kg.
Liming	200%	H_2O	2 m^3
	2. 5%	Na_2S (60%)	15 kg. (dry)
	1. 5%	NaHS(70%)	10 kg (dry)
	4%	$Ca(OH)_2$	40 kg
Washing	300%	H_2O	3 m^3
Fleshing, Trimming			
Washing	400%	H_2O	4 m^3
Basis: pelt weight, 1100 kg. (unsplit)			
Deliming, Bating	200 %	H_2O	2 m^3

	2. 5 %	Ammonium salts	27 kg.
	0. 8 %	Weak acids	9 kg.
	0. 5 %	Enzyme products	5 kg.
Washing	300 %	H_2O	3 m³
Basis: pelt weight, 750 kg. (ex- lime grain split)			
Deliming, Bating	200 %	H_2O	1.5 m³
	2. 0 %	Ammonium salts	15 kg.
	0.4 %	Enzyme products	3 kg.
Washing	300 %	H_2O	2. 2 m³

Basis: pelt weight, 195 kg (ex- lime flesh split)			
Deliming, Bating	200 %	H_2O	0. 4 m³
	1. 0 %	Ammonium salts	2 m³
	0.2 %	Enzyme products	0. 4 kg.
Washing	300 %	H_2O	0. 6 m³

TANNING			
Pickling	50 %	H_2O	0. 55 m³
	5%	NaCl	55 kg
	1 %	Acids	11 kg
Tanning	70%	H_2O	0.75 m³
	8 %	Basis chrome sulphate (25 % Cr_2O_3)	88 kg
	0.7 %	Basic agent Na_2CO_3 or MgO	8 kg
Sammying, splitting, trimming, shaving			
POST TANNING Wet Work- Grain Leather			
Basis: Shaved weight 262 kg			
Washing	400 %	H_2O	1 m³
Neutralisation	200 %	H_2O	0. 5 m³.
	1. 5 %	$NaHCO_3$	4 kg
	1. 5 %	HCOONa	4 kg
Washing	400 %	H_2O	1 m³

Retanning, dyeing, fatliquoring	100 %	H_2O	0. 3 m³
	5 %	Basic chrome sulphate (25 % Cr_2O_3)	13 kg.
	10 %	Organic tannins (75 %)	20 kg
	8 %	Fatliquor (70 %)	15 kg
	2 %	Dyestuffs (75 %)	4 kg
	1. 5 %	Acids	4 kg
Washing	600 %	H_2O	1. 6 m³
Vacuum drying			
POST TANNING Wet Work- Splits			
Basis: shaved weight, 88 kg			
Washing	400 %	H_2O	0. 35 kg
Neutralisation	200 %	H_2O	0. 2 m³
	1.5 %	Na_2CO_3	1.3 kg
	1. 5 %	HCOONa	1. 3 kg

Washing	400 %	H_2O	0. 35 m^3
Retanning, fatliquoring, dyeing	100 %	H_2O	0.1 m^3
	8 %	Organic tannins (75 %)	5. 3 kg
	10 %	Fatliquor (70 %)	6. 2 kg
	2 %	Dyestuffs (75 %)	1. 3 kg
	1. 5 %	acids	1. 3 kg
Washing	600 %	H_2O	0. 5 m^3
Vacuum drying			
FINISHING: The mass balance for finishing has been calculated on the basis of leather area; the composition pf coatings applied expressed as dry substance			
a) Grain (crust) leather, lightly corrected, 141 m5			
Impregnation (curtain coating):			
250 g/ m5, dry matter content 10 %		**Applied**	**On leather**
	Finish	35. 0 kg	-

	Solids	3. 5 kg	3. 5 kg
Base coat (reverse roller):			
1x 100 g/ m5, dry matter content 25 %	15 % loss		
1x 80 g/ m5, dry matter content 25 %	15 % loss		
	Finish	25.0 kg	-
	solids	6. 5 kg	5. 5 kg
Top spray (rotary sprayer):			
100 g/ m5, dry matter content 6 %	40 % loss		-
	Finish	14. 0 kg	-
	solids	0. 9 kg	0. 5 kg
b) Split (crust) leather 61 m5			
Base coat (reverse roller):			
1 x 250 g/ m5, dry matter content 10 %	15 % loss		-
1 x 80 g/ m5, dry matter content 10 %	15 % loss		-
	Finish	20. 0 kg	-

	solids	2. 0 kg	1. 7 kg
Top spray (rotary sprayer):			
100 g/ m5, dry matter content 20 %	40 % loss		-
	Finish	6. 0 kg	-
	solids	1. 0 kg	-