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LEATHER INDUSTRY

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CONTENTS

ABSTRACT

The tanning industry is known to be very polluting especially through effluents high in organic and inorganic dissolved and suspended solids content accompanied by propensities for high oxygen demand and containing potentially toxic metal salt residues. Disagreeable odour emanating from the decomposition of protein solid waste, presence of hydrogen sulphide, ammonia and volatile organic compounds are normally associated with tanning activities.

On the basis of yearly input ("soak") of about 6.8 million tonnes of wet salted hides and skins worldwide it can be estimated that about 3,427,000t of various chemicals are used for leather processing. A significant part of this amount is not actually absorbed in the process and is discharged into the environment.

With an average yield of 45-50 m^3 of wastewater per tonne of raw hide, the total amount of liquid effluent from light leather processing (almost 90 per cent of overall production) is over 300 million m^3 a year containing about 1,470,000 t of COD, 610,000 t of BOD, 920,000 t of suspended solids, 30,000 t of chromium and 60,000 t of sulphide plus more than 2,500,000 t of solid wastes (fleshing, wet blue splits, trimmings and shavings, buffing dust, etc). About one-half of that is produced in developing countries.

The substantial relocation of leather production from the industrialized to the developing countries which occurred between the 1960s and the 1980s ("The Big Shift") in effect moved the most highly polluting part of the process away from the OECD countries under pressure of increasing cost of labour and cost of effluent treatment installations and operations. This process was accelerated by a combination of restrictions in exports of raw hides and skins and various incentives for higher processing levels provided in developing countries.

Owing to the nature of the leather production, even in the most sophisticated tannery, technology remains to a certain extent a mixture of craft and science. While there are some typical phases followed in manufacturing, for example, the most widely produced chrome tanned shoe upper leather based on bovine hides (soaking, unhairing, pickling, tanning, retanning/dyeing, fat liquoring and finishing), strictly speaking there is no basic tannery process. As a corollary, it is not possible to simply replace the traditional technology with an entirely new "clean" process.

Since over 80 per cent of the organic pollution load in terms of BOD_5 comes from early wet processing, this is the primary target of most pollution control measures.

Among the low waste technologies possibly the most promising are: use of green hides from abattoirs without the necessity of temporary preservation; use of safe insecticides and biocides in curing hides and skins and wet blue leathers; hair-saving methods in the unhairing process; separation of unhairing and liming; recycling of unhairing and liming liquors; ammonium-free deliming; high chrome exhaustion systems; recycle and/or chrome recovery; chrome-free (alum) tanning whenever applicable, at least in the first phase of tanning; in finishing, at least base and middle coats should be made of aqueous polymeric dispersions and contain safe crosslinking agents. Computer control systems are being introduced in the newly industrialized countries.

Low waste technologies, generally speaking, require better skilled personnel and closer technical control than conventional processing. Thus, the lack of properly trained staff at different levels remains one of the crucial constraints. It is noted that each tannery's effluent treatment requirements need to be evaluated individually, not only according to the process being employed and the type of raw material being processed, but also according to the location of the tannery, the volumes of water being used and emitted and the direction of the emissions (surface waters, sewers, etc).

Typical tannery effluent treatment systems are described. Safe disposal of sludge which inevitably contains a certain amount of trivalent chromium causes considerable difficulties. Joint effluent treatment plants possibly combined with a central chrome recovery unit are often given as the optimum solution for clusters of tanneries found all over the world.

The main barriers to the adoption of more environmentally acceptable methods of leather processing and effluent treatment are the additional costs as follows: specialty chemicals required in reducing or eliminating the use of the main polluting chemicals; the cost of purchase and installation of water conservation devices, wastewater collection and reuse equipment; effluent treatment chemicals and process and effluent monitoring equipment; extra personnel and training to maintain technical control of low waste technologies and effluent treatment. Another factor is the traditional conservatism derived from hesitation over process alterations especially when satisfactory leather is being currently produced. This is particularly the case in small to medium scale semi-mechanized family owned units. Another barrier is the frequent remoteness of government-backed R & D facilities from everyday practicalities of leather-making, together with reluctance on the part of traditional tanner groups where resistance to change is compounded by political influence.

The beamhouse (unhairing) and the tanyard require cleaner technologies in leather processing. Also utilization of chrome-free solids as by-products and disposal of chrome containing sludge are possibly the main issues that need particular attention. However, legislation enforcement agencies lack skilled personnel to monitor performance of installed treatment plants.

The cost of introducing a cleaner processing method may be prohibitive and beyond reach of a small scale tanner: the price of a special drum for hair save unhairing with the necessary auxiliary equipment may be as much as twice the conventional drum. Enzyme unhairing needs very accurate control and consistency of all parameters (pH, temperature, float, etc) which is possible to achieve only in rather sophisticated tanneries and it is associated with higher production costs (partly off-set by lower wastewater treatment expenses). High chrome exhaustion tanning requires very expensive specialty chemicals, normally proprietary products.

Effluent treatment costs depend on specific site conditions, and vary within a very wide range. In Europe they are estimated to be of the order of US$ 5 to 15 per cubic metre of effluent or 4 to 6 per cent of the finished leather production cost. Initial treatment costs may not result in this level of on-cost in developing countries, but as standards in stringency and/or in enforcement advance they will inevitably increase.

Some recent examples from Africa indicate the cost of establishing a complete treatment plant for a medium scale tannery to be between US$170,000 and US$340,000.

Nevertheless, considerable strides in reducing pollution can be made by adopting measures which require little or no capital investment, such as:

- strict process control including avoidance of overdosing of chemicals typical for the tanning industry;
- "good housekeeping" - water conservation at all stages of wet processing;
- savings in chemicals by introducing reuse-recovery-recycle systems can pay for the simple equipment needed to run them, such as collection pits, pipes and pumps;
- introducing, as appropriate, some of the wide range of options of the low waste technologies mentioned earlier. (This will in effect reduce the amount of capital investment and the cost of operating the treatment system);
- maximization of returns on tannery by-products, residues from sludge and solid wastes (production of gelatine, protein powders and collagen for sausage casings and medical and surgical films, glue, animal feed protein and fertilizers, leatherboard, filter media, non-wovens, etc);
- establishment of a simple but well controlled and maintained treatment system (for example manually cleaned screen, equalization with aeration, clarifier, lagooning, sludge drying beds); joint effluent treatment plants for tannery clusters.

It is believed that by combining strict process control, good housekeeping measures and cleanliness, introduction of recycling of some floats, predominantly aqueous finishing together with simple treatment of wastes it would be possible to eliminate nearly 50 per cent of the total pollution load discharged into the environment with only marginal investment. If consistently applied in developing countries worldwide this would result in reduction of:

- COD, approx. 350,000 t/a;
- BOD_5, approx. 150,000 t/a;
- Chrome, approx. 10,000 t/a;
- Suspended solids, approx. 230,000 t/a.

A comprehensive, well synchronized action by respective governments, industry, R&D and establishments, environmental authorities, international organizations, etc. to address the main constraints mentioned earlier is a prerequisite to achieving ESID in the tanning industry.

Special soft term financing schemes for introduction of cleaner technology and installation of wastes treatment equipment is essential for many small and medium scale units in developing countries.

During the last few years pollution control has been given a very prominent role in UNIDO technical assistance to the leather and leather products industry so that at present there is virtually no project in the tanning sector without an environment component. Dissemination of information on environmental protection is another important area of UNIDO's activities in this sector.

1. INTRODUCTION

1.1. THE INDUSTRY'S GLOBAL PERSPECTIVE

The leather and its related downstream industries can claim to be the world's largest industrial sector based upon a by-product. In the case of leather, the raw material is a by-product of the meat industry. According to the Food and Agriculture Organization of the United Nations (FAO) statistics, taking the average of 1985/87, the value of the commodity under study with its downstream products was US$18.216 billion. It is estimated that if the value of other leather products were added to the US$20 billion figure, the full value could be between US$25 billion and US$30 billion. Hides and skins and their downstream products are vital earners of foreign exchange and they compare very well with the other agricultural commodities and, in fact, with any internationally traded commodities (see table 1).

1.2. ENVIRONMENTAL IMPACT

The significance of the tanning industry to the environment is the high volumes of wastewater discharged in the process of converting a putrescible animal by-product into a stabilized and marketable material. Whereas it is possible to process hides and skins successfully using about 15 l/kg, the calculated conventional volume is probably 30 l/kg while the realistic figure, given the often excessive quantities used in wash liquors, could be 45 l/kg. At this high level water usage globally by the tanning industry is of the order of about 350 million m^3/a.

1.3. HIDES AND SKINS PRODUCTION AND TRADE

1.3.1 **Dependence on the market for meat**

Availability of hides and skins is governed mainly by the demand for red meat. A governing feature of the leather industry is in the elastic nature of its raw material supply.

The bulk of bovine hides and ovine and caprine skins in industrialized countries are marketed to the leather industry and thus the number of heads slaughtered is roughly equivalent to the number of hides and skins available. A significant part of hides and skins is lost to tanners mainly in least developed countries in Africa owing to lack of marketing infrastructure, monopolies of various kinds or diversion into other uses such as food, tents, ropes, etc.

1.3.2. **World hide and skin supply**

Bovine hide is by far the most important raw material for the leather industry. The composition of world hide and skin supply up to 1987 is in table 2.

The most important determining factors are the animal population, the off-take ratio and the weight per hide and skin. While developing countries hold about 70 per cent of the world bovine herd they together continue to produce much less than half of the world hide output on a numerical basis. As the weight per hide on average is considerably higher in developed countries this disproportion grows in weight terms and output of hides in developing countries accounts for less than 40 per cent of the total.

The widest disparity between bovine population and output of hides occurs in Africa which accounts for more than 10 per cent of the world's cattle but for only 5 per cent of hide output. Africa offers the main prospect for increases in hide supply through reduction in current losses and improvements in husbandry and marketing. The region is subject to a UNIDO project which aims to assist in achieving these objectives.

Table 3 shows that world output of bovine hides and skins has risen almost 50 per cent during the last 20 to 25 years, reflecting improvements in cattle husbandry and expansion in beef production.

1.3.3. **Change in global pattern of demand for hides and skins**

The leather industry has expanded substantially in the developing countries during the past 25 years. Tanneries in the developed countries were once reliant upon raw materials from developing countries, but as the leather industry has grown in the developing world to give added value to their raw material resources, so the industry in the developed world has not experienced the degree of growth that has occurred particularly in S.E. Asia, China and Latin America. *A consequence of production expansion in some developing countries is that tannery input demands have outstripped locally available supplies and imports from the developed countries have become essential.*

1.3.4. **Change in volumes and direction of international trade**

Over 35 per cent of the output of raw bovine hides in 1987 entered international trade compared with 28 per cent 25 years previously. World shipments have risen by about 90 per cent. However, this expansion has taken place exclusively in developed countries, and developing countries as a group have reduced their exports of raw hides and skins by 60 per cent.

While developing countries as a whole were net exporters of raw bovine hides and skins in the early sixties to the level of 250,000 t, their net import requirements are now over 400,000 t w/s. This reflects the dramatic expansion in tanning capacity in most developing countries, but mainly in Latin America and Asia and the Pacific Region.

1.3.5. **End uses of leather based on different raw materials**

Bovine hides are the raw material for most shoe upper leathers, upholstery leathers and some garment leathers; heavy leather is always bovine. This category comprises mainly sole leather for shoes with lesser quantities of saddlery leather, case leather and a variety of industrial leathers. Sheepskin leather is used in garments, leather goods, bookbinding and gloving, while goatskin is also used for gloving, shoe upper and lining leather and leather goods. Pigskin is used in garments, leather goods, gloving and shoe linings.

1.4. THE PRESENT SITUATION

1.4.1. **Influence of high volume shoe manufacturing; high-tech leathers**

The overall picture that emerges of the world leather and leather products industry is one in which there has been massive transformation during the past 30 years. The higher quality European bovine hides have been an important resource to the *high-tech (automotive and upholstery) leather tanners* as they have supplied this growth market during the 1980s through to the present day.

During this 30 year period exports of hides from North America have increased and the finished leather industry has declined, the decline has largely occurred because of the massive level of footwear imports into North America, initially from southern Europe, but later increasingly supplemented by imports from East Asia. The exported hides have been turned into the leathers that have been imported back to North America in the form of footwear, garments and leather goods.

1.4.2. **Tanners in developing countries under pressure to invest in effluent treatment facilities**

The change of flow of international trade in raw material and the substantial relocation of leather production from the developed to the developing countries which occurred between the 1960s and the 1980s in effect moved the most highly polluting wet processing away from the OECD countries at a time when environmental regulations were beginning to bite in terms of cost of effluent treatment installations and operation. In many developing countries regulations were non-existent, or if they did exist, they were not strictly imposed. This undesirable situation in developing countries is now changing.

1.5. WHAT OF THE FUTURE?

1.5.1. **Influence of population growth and government policies**

Economic, political and technological developments in several industries impinge upon the future characteristics of the leather industry, covering all contingent industries from livestock agriculture to finished goods industries and the markets that they serve.

Population growth is another important factor. For example in China and India, where per capita incomes are rising faster than the world average, growth in the purchasing power of these rapidly increasing populations will be the dominant factor in the expansion of world demand for meat and for inexpensive leather goods. The fast growing, middle income populations of Asia will also constitute increasingly significant markets for higher quality leather and leather products. The demand for various luxury leather products, on the other hand, such as leather upholstered cars and high fashion garments, will depend on the growth and distribution of wealth in high income countries.

1.5.2. **Future hide and skin production**

Landell Mills Commodities Studies in their report 'The Leather Industry to the Year 2000' have reached the conclusion that for the world as a whole, hide production will increase by a total of 23 per cent (in weight), and skin production by 21 per cent, over the period from 1980 to 2000 (see table 4); most of this growth will occur in Asia and Latin America.

1.5.3. **Future demand for finished goods manufactured in leather**

The buoyancy of demand relative to supply is expected to maintain the long term, upwards pressure in prices of hides, skins and leather, especially in the quality sector.

Growth in the demand of leather footwear will be concentrated in lower income regions of the world: growth in China's demand for leather shoes is projected to more than double between 1990 and 2000. See table 5.

1.5.4. **Fragmentation of leather manufacturing among specialists**

The leather industry will continue to be complex and subject to a host of economic factors which can even force a change in its structure. The demands of the fashion market constrain the separation of finishing from the earlier processing. Tanneries usually have an enormous amount invested in work in progress. It is more capital efficient to subdivide the sequence at the points where the material is in a marketable condition. *Although there is resistance to relinquishing early wet-work processing, there is a strong case for specialization. Tanneries concentrating an early processing with concomitant investment in effluent treatment facilities are marketing semi-processed leathers in a range of specifications to leather dressers who take the leathers through to a ready-to-finish stage.*

The volume of raw materials available to the industry is increasing and will be processed into leather with the inevitable emission of effluent in the liquid, solid and volatile forms. The prospect of the global production of about 2,368.1 million m^2 (22 billion ft^2) of leather by the year 2000 presents a considerable challenge to the industry considering the toxic nature of some of the chemicals applied in leather processing and the volumes of aqueous media used.

While it is extremely difficult to make any reliable estimates, it is firmly believed that the existing gap between the supply of raw hides and skins and demand for various kinds of finished leathers will continue to grow (albeit with temporary oscillations). Leather, being perceived as a genuine natural material is expected to retain its appeal to the consumer. The man-made materials (simulated leather) are likely to dominate in low price bracket categories and/or as replacement of leather due to its non-availability.

2. ENVIRONMENTAL REQUIREMENTS FOR ACHIEVING ESID

2.1. ENVIRONMENTAL IMPACT OF THE LEATHER INDUSTRY

The leather sector is well known for its effluent problems. The polluting nature of tanneries is evident from the notorious odour that characterizes tanneries and tannery zones. While local populations are daily aware of the air pollution, local authorities are equally, if not more concerned about tanneries' liquid effluents which tend to be high in organic and inorganic suspended solids content accompanied by propensities for high oxygen demand and containing potentially toxic metal salt residues.

Treatment technologies in effect reduce pollutants in the liquid form and convert them into semi-solid or solid forms. So the pollution threat is being transferred from receiving waters to receiving land. Because sludge can affect the quality of soil and groundwater, it is understandable that local authorities and governments should be concerned that the disposal of sludge to soils and dry wastes to landfill should not adversely affect the fertility of soil, nor that metal salt residues, such as chromium, should inhibit crop growth in any way.

2.1.1. The elements of leather manufacturing

The tanning process

The objectives of tanning are to convert a putrescible hide into leather. Many alternative processes and materials are known and most tanners will use a variation of their standard process to change the type of leather they wish to make. For a schematic tanning process see figure I.

2.1.2. Environmental impact quantified

In order to assess this the magnitude of world production must be quantified. The globally comparable figures published by FAO in their latest (1989) statistical compendium are used for this purpose and are as follows.

	1985/87 average
World hide production input	4,926,600 t w/s
World sheepskin production input	934,000 t w/s
World goatskin production input	355,000 t w/s
World pigskin production input	600,000 t w/s

Approximate utilization of chemicals on the global level:

Computed in kg per 100 kg of wet salted weight (w/s), finishes in grams per square metre

	Heavy Leather 706,992 t w/s		Light Leather 6,108,808 t w/s	
	(%)	(t)	(%)	(t)
Lime	4.5	31,814.64	4.5	274,896.36
Sodium bisulphite	1.5	10,604.88	1.5	91,632.12
Sodium sulphide	3.0	21,209.76	3.0	183,264.24
Ammomium sulphate	2.0	14,139.84	2.0	122,176.16
Sodium chloride	6.0	42,419.52	8.0	488,704.64
Calcium formate	-	-	2.0	122,176.16
Sulphuric acid	2.0	14,139.84	1.5	91,632.12
Sodium Carbonate	-	-	2.0	122,176.16
Bating agent	0.8	8,837.40	0.8	48,870.46
Bactericides	0.1	706.99	0.1	6,108.80
Veg tans	35.0	247,447.20		
Chrome salts	8.0	488,704.64		

Total (rounded up): 391,314 t for heavy leathers and approximately 2,040,338 t of chemicals for light leathers.

Further computation: kg w/s x 0.75 = kg. wet blue
4,581,600 t wet blue

	(%)	(t)
Syntans	4	183,264.24
Veg tans	3	137,448.18
Fat liquors	4.5	206,172.17
Dyes	2	91,632.12
Dye Auxiliaries	3	137,448.18
Finishes 200 gm/m^2		
1,200.25 million m^2		240,045.00

In other words, **in the world, every year about 3,427,000 t of various chemicals is used for leather processing; a significant part of this amount is not actually absorbed in the process and is discharged into environment.**

<u>Amount of Pollutant per Wet Salted Hide Processed into Chrome Upper Leather</u>

One tonne raw hide yields approx 200 kg leather plus 50 m^3 liquid effluent (usual process water requirement is 25 to 80 m^3 water per tonne) containing up to 250 kg of COD, 100 kg of BOD_5, 150 kg of suspended solids, 5 to 6 kg of chromium and 120 kg of solids in sludge (the amount of wet sludge not less than 500 kg).

In addition there are in-plant solid wastes and by-products: untanned (120 kg of raw trimmings, 70 to 230 kg fleshing), tanned (115 kg waste blue splits, 110 kg trimming and shavings and dyed & finished (2 kg of buffing dust and 32 kg of trimmings) per tonne of raw hide.

On the above basis, for light leather production worldwide:

Liquid effluent	**305.44 million m^3**
containing approximately:	
	(million tonnes)
COD	1.47
BOD_5	0.61
Suspended solids	0.92
Chromium	0.03
Sulphide	0.06
Solids in sludge	0.73
plus	
Raw trimmings	0.73
Fleshing (120kg.)	0.73
Waste blue split	0.70
Trimmings & shavings	0.61
Buffing dust	0.01
Finished trimmings	0.19

Table 6 illustrates a typical untreated combined tannery effluent content.

2.2. LOW WASTE TECHNOLOGIES

2.2.1. **Variety of processes**

There is no basic tannery process. The variety of leather that can be produced is reflected in the variety and complexity of processes that are required. Heavy leathers for shoe soling and industrial use are subjected to long pit processes using vegetable tannin solutions. At the other extreme thin pickled sheepskin flesh splits are tanned by aldehydes generated by oxidizing fish oil in a hot air rotating drum. However the vast majority of hides and skins are chrome tanned in rotating process vessels. In examining low waste technologies, the preparation for chrome tanning in the beamhouse and the subsequent post-tanning processes on this substrate will be examined. The most widely produced leather is chrome tanned shoe upper leather based on bovine hides.

Processing is by batch and the size of batches is governed by the capacity of processing vessels. Drums up to 20 metric tonne capacity are the norm. Water usage varies between less than 20 l/kg. up to over 80 l/kg. The latest designs in processing vessels allow lower volumes of liquor. But many tanners prefer high float levels which produce the qualities of leather their customers require, particularly the fineness of grain. In all consideration of waste reduction it must be remembered that tanners compete in the market and therefore they are disciplined by what the market requires. A balance has to be achieved between reducing environmental impact and remaining competitive.

2.2.2. **Water conservation**

Reducing the usage of water through *low float processing* and operating batch rather than running washes does not perforce reduce the pollution load. It merely concentrates it in a smaller volume. Nevertheless there are benefits to reducing the quantity of water used. Costs for water are reduced. This is important where tanneries are served by a municipal supply. Batch washing in processing vessels is more controlled that continuous washing in drums with lattice doors and leads to greater uniformity of product. Low float processing improves the uptake of chemicals and consequently a reduction in chemical costs. A lower volume of water leads to a lower size of effluent treatment plant. *Water conservation measures lead to lower investment and operating costs. If such a policy is allied to the development of cleaner process technology with the recycling and the recharging of process liquors and the reuse of wastewaters where their influence on earlier processes is innocuous or even moderately beneficial, then there will also be a reduction in the environmental impact of the reduced volumes of liquid, semi-solid and vapour wastes that are emitted.*

Wash liquors from bating and neutralization can be *recycled* to soaking salted or green hides. The second lime wash can be the basis for a new lime liquor or as a soak where the alkalinity will accelerate the soaking.

Low float processing using 40 to 80 per cent water on the weight of goods, instead of conventional 100 to 250 per cent floats, has certain drawbacks. Friction within the goods and between the goods and the body of the drum can produce high temperatures which, particularly in areas of high ambient temperature, could endanger the quality of the leather. Coupled with this there is increased wear on the bodies and drives of processing vessels. Careful monitoring is essential.

Modern processing vessels are designed to permit savings in water and chemical usage through their actual design and internal structure and through the incorporation of controllable drainage and recycling systems and automated chemical dosing and injection systems. Manufacturers of such equipment claim that savings in chemical costs soon cover the cost of these vessels. These claims may well be justifiable.

However processes of certain types of material and in the production of certain types of leather require long floats. Dried hides have to be rehydrated in pits or paddles. Heavy leather processing which requires the gradual penetration of the vegetable tannins has to be performed largely in pits. Woolskin processing has to be done in paddles with mild surface agitation in order to avoid felting the wool.

2.2.3. **Curing hides and skins**

In developed countries hides and skins are either sprinkled with 30 to 50 per cent salt on raw (green) weight or they are brine cured by immersion in an agitated saturated salt solution which is maintained at a specified specific gravity in a raceway. In developing countries salt is often too expensive a commodity. Controlled shade drying is the usual method of preservation. Dried hides and skins are often dusted with insecticide. Derivatives of chlorinated aromatic hydrocarbons persist in wastes and are toxic to the environment. They are now prohibited in most European countries. **Pentachlorophenol, DDT, benzene hexachloride, dieldrin, arsenic and mercury based insecticides are either banned or severely restricted and listed in the International Register of Potentially Toxic Chemicals (IRPTC).** Relatively **safe insecticides are pyrethrum, permethrin, sodium silico fluoride and borax.**

Dried hides require large volumes of water to achieve rehydration. Salt from cured hides accounts for 60 per cent of the salinity of tanning waste water; a serious problem in countries where permitted salinity discharge levels are low.

2.2.3.1. *Process alternatives*

Where a tannery is close to a large abattoir, *green hides can be transferred to process without the necessity of temporary preservation.* Alternatively, *it is possible to chill hides and thereby preserve them without salt for a few days.* It is also possible to preserve raw material for several weeks after irradiation by electron beam or gamma rays. The latter two physical methods are not widely practised.

Amongst the chemical methods are preservation using gaseous sulphur dioxide, which is, in fact, unsuitable to working environments. Treatment with 1 per cent sodium sulphite and 1 per cent acetic acid in a 20 per cent liquor on hide weight, stored in a closed container will keep raw material for one month. Treatment with acid metasulphite and aluminium sulphate will preserve hides for four months. Boric acid cure lasts two weeks and shorter cures can be obtained with sodium chlorite or sodium fluorosilicate. Proprietary antifungal agents usually applied to wet blue material can also provide short term preservation of raw hides. *Commercial biocides with 5 per cent salt is another alternative, provided the agents are biodegradable.*

For developing countries the recommendation is the use of reduced quantities of salt. An application of 15 per cent will still provide six weeks preservation, while 5 per cent salt plus biocide can give two months preservation. For exporting, no long term preservation exists other than drying. Therefore the recommendation is shade drying and sprinkling with the insecticide pybuthrine.

The advantages of low waste preservation are the reduction of salt entering wastewaters from 150 to 200 kg/t down to 20 to 80 kg/t of hide and the absence of toxic insecticides and biocides. But the improvements are at the expense of the reduced effectiveness of preservation, the higher cost of innocuous insecticides and biocides and the need for rapid transportation.

2.2.4. **Beamhouse processes**

Over 80 per cent of the organic pollution load in BOD_5 terms emanates from the beamhouse; much of it is from degraded hide/skin and hair matter. 10 per cent comes from soak liquors, 70 per cent from unhairing/liming and 3 per cent from deliming and bating. The soak water provides 60 per cent of the salinity, the remainder comes from salt applied in acid and alkaline processes to suppress swelling of the pelt. Alkalinity and sulphide come from the liming/unhairing processes and ammonia nitrogen is generated during deliming and bating. The beamhouse is the source of all non-limed and limed solid wastes such as fleshings, trimmings and waste split.

2.2.4.1. *Soaking* is done in pits, paddles or drums sometimes using soak-assists such as 1 g/l sodium hypochlorite or 0.2-2 g/l sodium hydroxide or sodium sulphide and/or 0.5 to 2 g/l wetting agent, emulsifier, surfactant or enzyme preparation.

Liming aims to separate hair and loosen epidermal debris and surface pigmentation on the hide/skin at the same time swelling and opening the fibre structure so that soluble proteins and fats are removed. If a market for animal hair exists, then hair retaining processes are used. Wool is separated from sheepskins in developed countries in separate establishments known as fellmongeries. These establishments produce graded and scoured wools, pickled pelts and furrier grade woolskins for further processing into suede clothing woolskins (double-face) or rugskins. With certain types of skin, such as merino, the wool is more valuable than the pelt.

Heavy hides for heavy leathers are given seven day pit limings. Lighter hides and skins are drum or paddle processed for 18 hours in 200 to 400 per cent water on hide/skin weight with 2.5 per cent lime and 2 to 3 per cent sodium sulphide, if hair is to be retained (or a higher percentage of hair is to be dissolved - this method boosts the pollution load). Other chemicals used are sodium hydrosulphide and sodium hydroxide in small amounts. Dimethylamine sulphate was another liming auxiliary, but this is now deemed too environmentally toxic.

Goat and sheepskins are usually painted with a sulphide paste on the flesh side. The hair/wool is removed by machine and the pelts are then limed.

2.2.4.2. *Alternative methods*

In order to prevent degraded keratin from entering effluent streams, *hair-saving methods are recommended*. This can be done in pits or paddles using less sodium sulphide and mending the liquors instead of disposing of them. Careful analytical control is essential. Removal of hair is then performed by machine.

A drum or paddle process can be adopted using 100 to 200 per cent water and no more than 3.5 g/l sodium sulphide. The hair separates from the stock in solution, thereby avoiding a machine process and the hair is then filtered out by screening.

A succession of baths constitutes the 'Sirolime' process; firstly sodium hydrosulphide to loosen the hair, then sodium chlorate to oxidize the sulphide and finally lime to release the hair into the bath for filtering out.

Throughfeed systems spraying sodium sulphide and other chemicals have not gained wide acceptance, although the repeated use of solutions prevents high COD content in wastewaters.

Unhairing/liming liquors can be recycled after recharging, but swelling tends to reduce with successive cycles and so the fibre structure is insufficiently opened up. Measures such as acidification to pH 4, precipitation and separation of organic matter, collecting of hydrogen sulphide and reabsorption in caustic soda have been tried, but a better method is the *separation of unhairing and liming.*

In this method the sulphide unhairing liquor is recharged after filtration. The pelt is thoroughly washed and the waste wash liquor used for soaking hides. The pelt is limed with an addition of 0.1 to 0.3 per cent sodium hydroxide to control the swelling. This lime liquor can be reused after recharging. Over a 20 day period, sulphide can be reduced by 80 per cent, lime by 93 per cent, COD by 17 per cent and BOD_5 by 15 per cent in the wastewater compared with conventional liming.

Sulphide-free processing is possible but not widely practised. *The most promising method is enzyme unhairing using proteolytic enzymes.* For skins this can be accomplished overnight, but for hides it requires 1-2 days and is usually only 80 to 90 per cent effective, requiring a liming with sodium sulphide for 4 to 6 h afterwards. In any event, liming must follow enzyme unhairing in order to swell the pelt. Lime liquors can be recycled and all hair is retained.

The latest development in this field is the *pressure injection of enzyme solution from the flesh side* in a through-feed machine. This technology is still at an early stage.

For developing countries the recommendation for hides is the separation of unhairing and liming stages. Both liquors can be recharged and hair screened out. The intermediate wash can be reused as a soak liquor. Enzyme methods could be developed for skins. The clear advantages are reduced pollution load and reduced use of chemicals. The organic load emanating from the beamhouse can be reduced by 60 per cent. The use of enzymes can lead to the production of leather with cleaner and finer grains with less grain shrinkage. The commercialization of hair as a by-product offers a potential economic return. But all this has to be balanced with the need for recirculation equipment, screens, unhairing machines, the greater cost of specialty chemicals (especially enzymes), the capital, maintenance and technical control costs and the longer process times enforcing the capital cost of more work in process.

2.2.4.3. *Deliming and bating*

Removal of lime often involves the use of high volumes of water and chemicals in the process of reducing the alkalinity of the pelt. The application of acids to liquors and material containing sodium sulphide generates hydrogen sulphide gas, so it is necessary initially to oxidize the sulphide with sodium bisulphite or, less commonly, hydrogen peroxide.

Deliming chemicals in normal use are 0.5 to 2 per cent sulphuric, hydrochloric, lactic, formic or boric acids or acid salts, ammonium chloride or sulphate, or more recently by injection of gaseous carbon dioxide.

Deliming prepares pelt for bating by making it soft and permeable to liquids and air. Bating then removes the loosened epidermal debris i.e. the last vestiges of hair root protein, pigmentation and soluble collagen. Proteolytic enzymes applied in bating modify the elastin in the pelt, making the pelt soft, flat, in fact ready for tanning.

Bating is carried out in the same float. The length of the process depends on the thickness of the pelt. In the case of pelt for heavy leather, less deliming is required prior to vegetable tannage.

The most usual chemicals to use are sodium bisulphite and 1 to 2.5 per cent ammonium salts in a float of 50 to 150 per cent on pelt weight. The deliming proceeds with gradually increasing temperature, 20 to 37°C. The pH at the commencement of bating should be 7.5 to 8. Bate compounds contain ammonium salts to prolong the deliming action and wood flour as carrier for the enzyme. This combined process generates 40 to 70 per cent of ammonia nitrogen in tannery effluents.

Yet **it is possible to delime without using ammonium salts.** Hydrochloric acid with sodium bisulphite, sulphuric acid with magnesium sulphate, proprietary products based on esters of carboxylic acid (usually 1 to 3 per cent offered) can bring the pH down to 7-8 range. Carbondioxide injection requires assistance from a small quantity of either ammonium sulphate or a salt of a polycarboxylic acid. *There are ammonia free bating agents available.*

Bating is carried out using 0.05 to 0.7 per cent bating agents, usually comprising proteolytic enzymes of the pancreas or of bacillus subtilis and performed at pH 8 to 9 and 20 to 37°C.

Tanners in developing countries could use ammonia-free deliming-bating processes provided strict controls are kept. In order to prevent release of hydrogen sulphide, oxidation with bisulphite should be applied. Carbon dioxide deliming requires precise technical control and investment in special injection piping. Speciality proprietary products will increase costs.

2.2.5. **Tanyard processes**

2.2.5.1. *Pickling*

Pickling adjusts the pH of the pelt prior to tanning at the same time sterilizing enzyme activity. Chemicals employed are 5 to 10 per cent salt or sodium sulphate, 0.6 to 1.5 per cent sulphuric, hydrochloric, acetic or formic acids and a small amount of *fungicide; thiobenzothiazol is recommended rather than paranitrophenol, tri-or penta-chlorophenol, B.naphthol, parachlormetacresol or mercury fungicides which are all too toxic.*

2.3.5.2. *Degreasing* is necessary for very greasy hides and skins. Hides from cattle reared in feed lots tend to carry much grease. Sheep and pig skins also tend to be greasy. Solvent degreasing leaves a problem with disposal or greasy residues after solvent recovery. *The alternative is to abandon solvent recovery and dissolve greases with surfactant.* Thus grease and surfactant are transferred to wastewater and consequently only biodegradable surfactants should be used. If possible, it is preferable to install a separate effluent collection system in order to prevent greases and surfactant being discharged.

Degreasing can also be applied after tanning, in which case it is more usual to use a solvent system with recovery facility using white spirit, kerosene, monochlorobenzene or perchlorethylene. This is usually applied to sheepskins.

2.2.5.3. *Tanning*

Seventy to 80 per cent of leather produced in the world is processed in its main tannage with basic chromium sulphate. The tannage begins in the pickle bath. This may consist of 40 to 60 per cent water with 5 per cent salt, 1 per cent formic acid or calcium formate and 1 to 1.8 per cent sulphuric acid. Pickling time may be 0.5 to 2 hours depending on the thickness of the pelt.

The chromium salt, usually basic chromium sulphate is added in quantities ranging from 8 to 12 per cent, along with other chemicals such as sodium formate or phthalate masking agent, a salt of a dicarboxylic acid to enhance chrome uptake and 0.1 per cent fungicide if storage or sale in the wet blue condition is envisaged. The process is basified using 1 per cent sodium bicarbonate, magnesium oxide or sodium carbonate. Alternatively it is possible to use self-basifying chrome powders. At the end of the process, which may take 6 to 24 hours, the pH is 3.6 to 3.8 and the temperature 35 to 38°C.

Effluent from chrome tanning can contain 60 to 90 kg. neutral salt per tonne of hide, equivalent to 25 per cent of salt in the whole effluent. Chrome content of effluent may be 8 to 12 kg of chrome oxide per tonne of hide or 4 to 5 g/l from a 100 per cent float. Solid wastes at the end of this stage include chrome leather shavings and trimmings and waste split.

2.2.5.4. *Alternative methods*

Low chrome systems using only 5 to 6 per cent chromium sulphate require a pretannage, possibly using an aluminium salt. This approach has the advantage of producing a pretanned leather in a *wet white condition* rather than wet blue. In this condition the leather can be split and shaved, thereby eliminating chrome from waste split and shavings. The leather can be stored in this condition for up to six months and can be traded as a semi-processed leather. Aluminium in effluent and solid wastes, however, is not without its problems as aluminium is known to be more poisonous to aquatic life that trivalent and even hexavalent chromiums under certain conditions.

Production of wet white as a preliminary to main tannage in chromium or other tanning agents has not been adopted to any extent by the leather industry. As a main tannage aluminium is unsuitable because it is not sufficiently resistant to water and perspiration i.e. the tannage is reversible.

High exhaustion systems or reuse (recovery and recycle) systems are probably more realistic that the change to alternative tanning materials. There are grounds for accepting that the ecotoxicity of chromium is low.

The principal fear is that in the environment trivalent chromium will oxidise into its hexavalent form. If such oxidation occurs under natural conditions it is reversible. Trivalent chrome salts do not irritate the skin, they are neither mutagenic nor carcinogenic. Their toxicity to fish, bacteria, algae, higher plants etc. is relatively low. In water, trivalent chrome salts are usually converted into chrome hydroxides. These age and become less and less soluble, with only small proportions remaining in solution. Only a small amount of trivalent chromium can be absorbed from the soil by plants, so chromium does not accumulate in the food chain. Chromium is an essential trace element. A chrome deficiency in humans and animals can impair physiological processes leading, for example, to certain types of diabetes.

Alternative mineral salts such as aluminium, zirconium, titanium and iron are possible substitutes for chromium salts. Basic aluminium chlorides, sodium aluminium silicates and zirconium sulphates have definite value as retanning materials at the stage, following the main tannage, when different tanning materials are applied in order to confer the desired final character to the leather.

Recently titanium compounds, especially ammonium titanyl sulphate and magnesium-aluminium-titanium complexes have been developed as alternatives to chromium in the main tannage. But leather produced with these salts so far have not matched the properties and qualities of chrome leather. That is not to say that titanium has no future. It is useful as a pretan, a combination tan and retan. In combination with syntan it produces a good substrate for dyeing pastel shades and produces a good nap on suede.

Iron tannage can be discounted because of the poor properties that are imparted. Zirconium and titanium salts produce acceptable leathers and they appear to be ecotox-icologically acceptable, but the leathers have lower shrinkage temperatures than chrome leathers and therefore could not withstand the temperatures applied to leather in modern shoe-making processes.

Certain organic compounds could replace chromium as tanning agents. However these are isocyanates and aldehydes and fall short of occupational hygiene regulations. In western Europe working environments should not contain more than 1.2 mg/m^3 formaldehyde and 0.8 mg/m^3 glutaraldehyde.

High chrome exhaustion systems coupled with a reuse system offers the best route to reducing the pollution load from the tanyard. Salt can be partially replaced in the preliminary pickling process with a non-swelling acid such as phthallic. This allows a reduction in the chrome offered because the organic acid creates the conditions for good distribution of chrome throughout the substance of the leather. Higher temperatures and longer process times are applied than in conventional tanning. From a pickle temperature of 30°C, the tanning temperature should rise to 40°C and the final pH should be between 4.0 and 4.7. Temperature is related to the volume of the float and the rotating speed of the process vessel so care is needed. Short floats should be used wherever possible, always bearing in mind that friction can damage grain quality. Auxiliaries that mask the reactivity of the chrome allow the achievement of good penetration, gradual basification and good fixation of the chrome onto the pelt. Appropriate auxiliaries are aliphatic dicarboxylates, polyamides, aluminium silicates and polyphosphates. Chrome fixes to the reactive carboxyl groups of the protein collagen, the main constituent of hide/skin. There are reactive amino groups and, in order to increase chrome uptake and fixation, it is possible to fix aldehyde carboxylic acids to the amino groups leaving the carboxyl group free to fix more chrome. Glyoxylic acid applied in the pickle liquor can provide this advantage.

Good fixation is critical otherwise chromium may be released during subsequent mechanical and wet processes. In effluent from conventional systems only 60 per cent of the chrome comes from the tanning liquors while 20 per cent comes from draining and wringing (sammying) and the remaining 20 per cent from the combined post-tanning wet processes of retanning, dyeing and fat liquoring.

The results from such applications are an 80 to 98 per cent exhaustion of chromium from the liquor, a reduction of chromium in liquid effluent of 10-40 mg/l compared with 100-300 in conventional tanning. In terms of weight of material in process, waste chrome in effluent in conventional processing is 8 to 12 kg/ton hide. This reduces to 0.2 to 0.5 kg/t (figure II). However, the cost of specialty, high chrome exhaustion proprietary products is considerably higher than of conventional chrome salts.

After separate collection of waste liquors from tanning, draining and sammying, the tanning and draining wastes are filtered and reused in tanning. The sammying waste is filtered and used for pickling. Using such a system chrome exhaustion has been proved to increase from 60 to 70 per cent to 95 per cent and chrome savings have been 25 per cent.

Recovery of chrome, prior to recycling, requires the precipitation of chrome with alkali, possibly with addition of organic flocculant and temperature adjustment to accelerate settling. After filtration the supernatant liquor can be discharged, while the precipitate is redissolved in sulphuric acid and adjusted to the required basicity. It should be noted that difficulties may be encountered in precipitating masked chrome complexes. Although more expensive than caustic soda, sodium carbonate or calcium hydroxide, magnesium oxide is considered the best precipitating chemical. (Figure III Chrome Recovery).

There are difficulties in applying chrome solution where a powder system is operative, therefore it may be preferable to base split tannage on recovered chrome, assuming, of course, that splitting has taken place in the limed condition.

Reductions in chrome emitted can be from 8 to 12 kg/t hide down to less than 1 kg/t.

Developing countries could move to high exhaust systems, given the maintenance of good technical control.

The obvious advantages of these process modifications and reuse systems are increased utilization of chromium and a consequent saving on chemical costs and effluent treatment cost. The drawbacks are the expenditure on sophisticated chemicals, special equipment for screening, filtering, precipitation and circulation and monitoring equipment for precise technical control.

Recommendations concerning chrome tannage for the future could be for a replacement of chrome at least in the first phase of tanning. Despite low ecotoxicity, authorities throughout the world are toughening their regulations on chrome in liquid effluents and in sludges for dumping. Chrome free solid wastes from splitting and shaving would be produced and liquid discharges reduced. In the second tanning phase chrome could be applied in combination with aluminium, titanium, vegetable tan or aldehyde, or a pure chrome high exhaust system could be applied. In each case chrome discharge would be reduced.

Developing countries would be well advised to consider wet white processing using a masked aluminium salt. Despite problems with toxic effects on fish and aquatic organisms and high neutral salt emission, a reduction in chrome emission may be enforced by local legislation. Production of wet white could reduce chrome utilisation by half. There would be no chrome tanned solid wastes. The high fixation and low toxicity of titanium may result in these salts superseding aluminium in the production of wet-white.

There are disadvantages which must be acknowledged. Process times are longer, chemical costs are higher, splitting and shaving are more difficult in the wet white and the character of the final leather becomes fully dependent on the second phase (main tannage) and third phase (retannage) of tanning.

2.2.5.5. *Vegetable tanning* is normally applied to heavy hides for the production of sole or industrial leathers, it is also still applied in developing countries to bovine hides and skins, sheep and goat skins in order to bring them into a 'crust tanned' condition, an intermediate stage at which they are a marketable commodity.

Tanning is performed in pits in a counter-current system, the pelt entering the weakest liquor and progressing, pit by pit, to the strongest liquor. Such systems produce leather in up to five weeks, depending on the substance of the pelt. Rapid tanning can be achieved by pretanning in a polyphosphate to assist subsequent penetration of the tanning material. In this way the pit process can be reduced to between 20 to 25 days. The vegetable tanning process is then completed in a drum in strong liquor. Sole leather requires 33 to 40 per cent tanning material on pelt weight, industrial use of leather 28 to 30 per cent, crust tanning 15 to 20 per cent.

Vegetable tannins are naturally occurring polyaromatic materials, divided into hydrolysable and condensable types. The most important are mimosa bark and quebracho wood (condensable) and chestnut, valonea and myrabolans (hydrolysable). Effluent is created from the drain-off from the weakest liquors as the strongest liquors are recharged. It is turbid effluent causing dark colouration to the mixed emission and contains a higher load of poorly biodegradable COD than chrome tanning liquid waste.

Alternative vegetable tanning methods are closed systems which ensure high utilization of material. The 'Liritan' process developed in South Africa consists of a pit pretannage for two days using polyphosphate and sulphuric acid until penetrated, followed by a pit pretannage for two days in weak veg liquor, followed by three days in a counter current system at 35°C and then finishing off in a drum at 40°C with a 45 per cent tan offer. This process takes 12 days and utilizes 97 per cent of the tan applied.

The advantages of such processes are high chemical uptake, low pollution load, uniform penetration of the veg tan and shortened process time with consequent financial efficiency. Again, a disadvantage is the necessity of careful technical control.

2.2.6. **Post-tanning wet processes**

Retanning, dyeing and fat liquoring are usually carried out as a sequence in the same processing vessels. If vegetable tans are used, 2 to 3 per cent of the shaved weight are applied. Syntans are often combined with veg tans because they have a dispersing effect and improve the distribution of the veg tans throughout the substance of the leather. Syntans are often used on their own. They are sulphonated products of phenol, cresol and naphthalene and resins from polyurethanes or polyacrylic acids. They are used for filling as well as tanning and contribute to the final characteristics of the leather. Resins are often applied at this stage as fillers, urea formaldehyde and dicyandiamide condensates being good examples.

Exhaustion of retanning agents is mainly a question of quantity, time and pH and therefore the right combinations will lead to satisfactory results as long as the products are not toxic. As syntans react with proteins, ecological problems can be reduced if they can be partially replaced by less astringent filling agents. Sensitive protein in fish is virtually tanned in concentrations of 5 mg/l of an astringent phenol syntan. With less astringency, the lethal level is raised to between 50 and 200 mg/l. Bacteria in biological treatment plants are proteinaceous consequently waste astringent syntan will block their activity. It is therefore necessary to know the toxic effect on bacteria where wastewaters will be treated in such systems.

Tanners normally process for high exhaustion of dyes and fat liquors, not least because of the disciplines of maintaining shade consistency and fat distribution batch by batch, but also the high cost of these agents deters wastage. The process of dyeing and fat liquoring involves acidification of the float in order to fix these materials, but the lowering of the pH below 4 has the effect of releasing chromium into solution. This problem underlines the necessity of achieving very good fixation of the chrome compounds during the tannage.

The addition of amphoteric polymers can greatly improve the exhaustion of dyes and fat liquoring agents. Although this represents additional organic substance entering the system, significant reductions in COD can be achieved, polymeric auxiliaries can be tailor-made to impart desirable properties to leather. Not only does this ensure high fixation of other agents, but polymeric auxiliaries themselves can also function as retanning and fat liquoring agents and thereby reduce the pollution load.

Dyeing is normally carried out using 1 to 6 per cent acid, direct, basic, pre-metalized or speciality dyestuff. Fat liquoring involves the application of 3 to 10 per cent raw, sulphated, sulphited fish, vegetable or animal oils, mineral oil or synthetic oils.

2.2.7. **Finishing**

2.2.7.1. *Conventional finishing*

Conventional finishing comprises of all or a selection of the following: colour spray, applying colour to undyed leather or adjustment to the dyed colour of leather using dye dissolved in solvent; grain impregnation with a polymeric dispersion diluted in solvent to penetrate and improve the firmness and smoothness of the surface - acrylates are most commonly used; base coat, consisting of a polyacrylate, polybutadiene or polyurethane binder with pigments and auxiliaries to ensure good surface colour and adhesion; if the leather is semi-aniline an effect colour is sprayed; final coat, consisting of a nitrocellulose or polyurethane lacquer.

Proposed legislation to control the emission of volatile organic compounds has stimulated the development of water-based alternatives to solvent based finishes which have mainly been the top coat lacquers.

There is a need to eliminate hazardous crosslinking agents used to improve abrasion and rub resistances in acrylic and polyurethane dispersions.

Conventional spray equipment is wasteful. Between 30 and 50 per cent of finish can be lost whereas, using a roll coating machine, losses may be as low as 5 per cent. Exhaustion from spray machines and drying tunnels can be improved by efficient scrubbing to clear the air emission.

An overview of maximally admissable concentrations of gaseous harmful substances in the working atmosphere (daily exposure 8 hours) is shown in table 7.

2.2.7.2. *Improved methods*

Without the introduction of solvent-free finishing a large tannery could be evaporating 250 kg solvent per hour, half from the spraying machines and half from the driers. Final lacquers may contain 90 to 150 g solvent per m^2 leather. *To reduce health and safety hazards base and middle coats should comprise aqueous polymeric dispersions containing safe crosslinking agents.* Isocyanates and aziridine are no longer recommended; epoxides and carbodiimides are preferable at the rate of 1 to 10 per cent epoxide with polyacrylate and 1 to 10 per cent carbodiimide with polyurethane binder dispersions. Alternatively, self-crosslinking reactive polymers containing N-methylolamide groups can be used.

An interesting development which may gain greater acceptance is the *use of finishes devoid of organic solvent or water*. They consist of prepolymers, reactive monomers, photoinitiators, photoactivators and pigments. The finishes are crosslinked by electron beam (EB) or ultra violet (UV) radiation. This system is particularly suited to finishing cut components for shoes. Another interesting possibility is the injection of liquid carbondioxide into a coating. In this way two-thirds of solvent normally used can be eliminated, but the equipment and licensing are expensive.

For pigment dispersions, products containing cadmium, lead and hexavalent chromium are the most worrying. Organic alternatives are now available equivalent to lead chromate and cadmium sulphide in all except covering power. But this can be compensated for by the inclusion of colourless fillers in the finish formulation.

Top coats should be mainly aqueous requiring minimal solvent. For example, a nitrocellulose based water-soluble emulsion contains 14 per cent dry matter, 56 per cent solvent and 30 per cent water. When diluted 100 per cent with water, the solvent component falls to 28 per cent i.e. 20 to 33 g/m^2 leather instead of 90 to 150 g/m^2.

Alternatively a system where nitrocellulose is partially replaced with polyurethane or polyacrylate dispersions i.e. a system with 12 per cent solvent, 10 g/m^2 can be used.

It would be quite feasible for tanneries in developing countries to apply aqueous finishes for base and middle finish coats and to apply aqueous nitrocellulose with polyurethane or polyacrylate top coats. Environment-friendly crosslinking agents or self-crosslinking reactive polymers could also be incorporated. Roll coating does not offer insurmountable technical problems. Benefits are felt from the reduction of VOCs in the workplace and financial savings accrue from the adoption of roll coating. The disadvantages are higher chemical costs and changes in the physical properties of finishes, which can be compensated by judicious reformulation of finishes.

2.3. EFFLUENT TREATMENT TECHNOLOGY

It need be no surprise that papers presented at leather industry conferences nowadays are primarily concerned with 'green' process technology, reuse and recycling systems and waste treatment. There is an abundance of technical literature revealing that the leather industry in the developed world has responded well to the environmental challenge.

It has been recognised that 'good housekeeping', process modification, reuse and recycling systems yield cost savings, while effluent treatment creates on-costs.

2.3.1. **Mode of treatment governed by process and tannery location**

Inevitably there must be effluent requiring treatment and this must comply with local regulations on emissions. It should also be stressed that every tanner's emission problems are individual, **there is no standard tannery effluent**. This reflects both the great diversity of leather production and the fact that the raw material itself is not uniform. Thus every **tannery's effluent treatment requirements need to be evaluated individually, not only according to the processes being employed and the type of raw material being processed, but also according to the location of the tannery, the volumes of water being used and emitted and the direction of the emissions (surface waters, sewers etc.).**

A tannery located in open country where there is space for lagoons may be the best means of treating effluent and reducing it to sludge. In urban areas, where space is at a premium, more sophisticated measures may be needed in order to create effluent for disposal to municipal sewers. Odour and noise may require special measures also. In many countries there has been a tradition for tanneries to develop in zones. **Where tanneries operate in close proximity to one another common effluent treatment offers definite advantages.** Typical wastewater discharge standards are shown in tables 8 and 9.

2.3.2. **Effluent treatment sequence**

As mentioned earlier, there are virtually no two identical tanneries, and, as a corollary, every effluent treatment plant is tannery and site specific. In general it consists of the following steps:

(a) Pretreatment: it involves screening to remove coarse material which would otherwise block pipes and pumps.

(b) Primary (Physico-Chemical) Treatment: Usually it deals separately with sulphide containing liquors from the beamhouse and chrome floats from the tanyard, followed by equalization of the flow of effluent streams, dosing of coagulant (for example alum) and flocculant (polyelectrolite) to facilitate sedimentation of suspended solids which takes place in clarifiers resulting in removal of the major part of BOD; sludge evacuated from the clarifier inevitably contains some chrome.

(c) Secondary (Biological) Treatment: there are many options ranging from different types of lagooning (facultative, aerated,anaerobic), trickling filters to oxidation ditches or a combination of them.

(d) Tertiary Treatment: gradually introduced in countries with strict ammonia nitrogen discharge limits: very sensitive biological processes like nitrification and denitrification required.

(e) Sedimentation and Sludge Handling. Sludge may have to be dewatered before disposal. Increasing limitations on the use of chrome containing sludge in agriculture and disposal to landfill sites are bringing greater problems to the industry, despite considerable achievements in reducing levels of chromium in sludges.

All treatment facilities must beware of the dangers of seepage which can pollute groundwater.

2.3.2.1. *Pretreatment: Screening*

Screens are simple enough to be produced locally. Self-cleaning screens such as mechanical rotating screens are available which can separate 30 to 40 per cent of suspended solids from raw waste.

Settling. A preliminary settling can separate out up to 30 per cent COD, much of it in the form of organic solids. This provides an ultimate saving in the use of flocculating chemicals and a consequent reduction in sludge volume.

2.3.2.2. *Primary treatment*

Primary treatment involves physico-chemical processes which remove the bulk of the main pollutants, BOD, COD, sulphide and chromium. (Figure IV).

Sulphide. Neutralization of alkaline liquors from the beamhouse causes the release of gaseous hydrogen sulphide. Therefore it is essential to treat this effluent before it is mixed with mildly acidic tanyard effluent. Catalytic oxidation and direct precipitation are methods that are favoured by tanners.

(a) Catalytic Oxidation is usually performed in an aeration system using a daily application of a manganese catalyst to prevent bad odour emission from the liquors. If performed in a tower, air is blown in at the base through diffusers. But for large volumes of effluent, surface aeration in a tank is more usual. Foaming is prevented through addition of an anti-foaming agent or kerosene. Analysis of beamhouse effluent has to be done regularly, in order to adjust dosages of air and catalyst. Air contains 0.28 kg. oxygen per m^3 and 1 kg. sulphide require 0.75 kg oxygen to convert it to sulphate. A normal injection would be 60 m^3 air per m^3 effluent with a manganese catalyst concentration of 100 mg/l at a process pH of 10. This method is not suitable for liquors being transferred to anaerobic lagoons as sulphide will regenerate in these conditions. Sulphate is imperfectly formed so if liquors are allowed to stand sulphide reforms.

(b) Direct Precipitation can be achieved using ferrous sulphate and ferric chloride. But this is usually only applied to equalized effluent because precipitation of hydroxides reduces the pH. The precipitate is dark in colour and, if inefficiently sedimented, gives a dark coloured effluent and a large volume of wet sludge.

Chromium will, ideally, be vastly reduced through the adoption of high exhaustion tanning systems and/or reuse-recovery-recycle systems. Any chrome remaining from wash liquors and from the retan/dye/fat liquor float can be raised in pH to 8 with lime, then treated with 200 ppm aluminium salt plus 5 ppm anionic polyelectrolyte to produce a flocculate which is then separated out in a sedimentation tank. The supernatant liquor is then passed to further treatment after equalization with beamhouse effluent.

Flow Equalization is necessary in order to avoid excessive peak flows from either beamhouse or tanyard. It is done after removal of sulphide and chromium so that these separate waste streams are not diluted before treatment. Balancing tanks should hold one day's effluent and should not fall below 30 per cent of total capacity in order to ensure sufficient volume to equalise inflowing effluent.

Equalization causes some neutralization and mutual precipitation, but suspended solids should not settle and aerobic conditions should be induced though mechanical agitation or air injection through a submerged diffuser. This promotes flocculation so that in the subsequent physico-chemical treatment a greater volume of solids settles out.

A tank 2 to 4 m deep should have an air injection of 3-4 m^3/h per m^3 tank. Power requirement is about 30 W/m^3 liquid.

Physico-chemical Treatment for BOD and Solids Removal

As much as 95 per cent of suspended solids and 70 per cent BOD can be removed by coagulation with aluminium and flocculation with 1 to 10 mg/l anionic polyelectrolyte. The dosage is governed by the character of the effluent and the degree of clarification required.

In some cases clarified effluent with a very low pollution load and with very low salt levels can be used for irrigation of land where water is in short supply. Effluent containing not more than the figures given below might be acceptable:

Total dissolved salts	500 g/m^3
Sodium absorption ratio	5
pH	4.5-9.0
Chromium	0.1 g/m^3 and 50 g/ha total mass

2.3.2.3. *Secondary treatment*

The chosen system must withstand shock loads, power losses and other contingencies therefore biological filters are unsuitable. Activated sludge containing a concentration of aerobic bacteria and other micro-organisms is a preferable system for reducing the quantity of sludge.

<u>Low load activated sludge</u> is particularly suitable for treating tannery effluent. This is performed in an oxidation ditch with a 2 to 4 day retention and low organic loading which can withstand shock loads. The biological activity of the sludge is maintained through additions of phosphate and the nutrient level can be maintained with 10 kg. Fertilizer containing 18.5 per cent phosphorous pentoxide per 100 m^3 effluent per day. Effluent with a BOD_5 level as low as 10 mg/l can be produced in this way.

Where space is limited high rate activated sludge can be used. This is a continuous oxidation of effluent in an energy intensive system, using 1 kW/kg. BOD_5 in a retention time of 6 to 12 hours. This system is sensitive to shock loading and is therefore less suitable to developing countries where less control would be inevitable.
In rural areas effluent can be lagooned. There are five types:

(1) Anaerobic lagoons can remove 85 per cent BOD_5 in 10 days, but they tend to be air polluting because sulphide reforms and some is given off as hydrogen sulphide gas. Cost is low, but these are only suitable for remote locations.

(2) Facultative lagoons have an aerobic layer above the anaerobically decomposing waste. Less odour is given off and they can be designed to use natural photo-synthesis. However they are subject to climatic variation and are therefore difficult to control.

(3) Aerated lagoons require mechanical surface aerators with a power consumption of 10-30 W/m^3.

(4) Facultative aerated lagoons can reduce BOD_5 down from 660 mg/l to 90 mg/l at 2 W/m^3 in nine days. Biological purification is achieved through the agitation keeping solids in suspension.

(5) Evaporation lagoons are suitable to dry, warm climates. They are governed by rates of evaporation and unless extensive in area, they become malodorous.

2.3.2.4. *Tertiary treatment*

Nitrification/denitrification reduces the nitrogen load. This helps to decrease the eutrophication of inland water. However these systems are expensive to install and operate and alteration of beamhouse processing, especially deliming, to exclude ammonia nitrogen from effluent is a better option.

2.3.2.5. *Sedimentation and sludge handing*

Horizontal flow tanks are cheap, but they are inefficient unless mechanically scraped. When the tank is nearing its capacity in sludge, the effluent will pass over the surface without sedimenting.

Vertical tanks are preferable to horizontal ones. Constructed in steel, fibreglass, concrete or wood, they need to have 60° lower part wall angles in order to induce self-desludging. Turbulence at the inlet will ensure mixing and encourages flocculation. The turbulence must only be at the surface otherwise the settling of solids to the base will be hindered. Settled sludge is drawn off by gravity from the base while clarified effluent flows off the top.

Flotation is yet another method for removing suspended solids from mixed effluent. Air is dissolved in the incoming effluent under pressure. In the treatment tank minute air bubbles carry suspended solids to the surface. Air bubbles can also be created by the electrolysis of the effluent. Solids are skimmed off the surface in this system.

Sludge normally containing only 3 to 5 per cent solids can be discharged by gravity or pumped to a tanker. Sludge volumes need to be calculated in order to ensure that treatment plant and storage facilities are of sufficient capacity. For instance, 400 m^3 effluent per day containing 3300 mg/l suspended solids with a clarification efficiency of 95 per cent will yield 1,250 kg/d of dry solids which is equivalent to 30 m^3 sludge slurry at 4 per cent solids content.

In order to reduce sludge volumes, dewatering is necessary. This can be done by:-

(1) Drying. Sludge can be thickened to a 10 per cent solids content in one day using a coagulation/flocculation agent such as lime or ferrous sulphate with a polyelectrolyte. It is then transferred to a drying bed comprising layers of filter media and the surface sprinkled with lime to inhibit generation of odour. This is a cheap method but it requires manual removal of the sludge from the bed when it has dried to 25 to 30 per cent solids content. The sand layer in the drying bed which lies above the inclined gravel bed is removed with the sludge and has to be replaced with every load. The drying time is 2 to 4 weeks.

(2) Pressing by belt press rather than high capital cost filter press can dewater sludge down to 20 to 30 per cent solids. This is suitable for tanneries producing more than 400 m^3 effluent per day. If the content of sulphide and chromium is within acceptable limits, tannery sludge being largely organic, can be used as an agricultural soil conditioner or fertilizer.

The nitrogen present provides fertilization properties. It is recommended that it be ploughed in quickly in order to avoid the formation of a skin on the soil surface. The sludge should be in an aerobic state.

Sludge can also go to landfill. This needs careful control and it must be covered with inert material in order to prevent odour and insect infestation. Moderate quantities of sludge containing trivalent chromium are unlikely to cause problems. Fears of conversion to the toxic hexavalent form are unfounded, nevertheless many local authorities are nervous about accepting it (See tables 10 and 11).

Landfills already receiving acidic waste may be unsuitable for the disposal of tannery sludge because reactions could possibly cause the liberation of hydrogen sulphide gas and chromium containing sludge could dissolve to liberate soluble chromium which could leach through to groundwater.

Tighter regulations on landfill are causing consideration of incineration. This requires very careful operation in order to prevent unacceptable hot air emissions which would not meet the standards set in air pollution regulations. Ash containing soluble metals is a major concern.

2.3.2.6. *Advanced treatment systems*

These can be tailored to specific circumstances and the quality of effluent required. These systems are expensive and require expert control. It is advisable to alter processes and chemicals utilized and thereby avoid the costly sophistication of such methods as:

- high performance aeration
- nitrification/denitrification
- high efficiency filtration
- carbon filtration to remove pesticides and other organic materials
- reverse osmosis (to reclaim water)

2.3.3 **Recovery of residues and wastes**

Biogas can be recovered by the digestion of sludge. Carbon dioxide and hydrogen generated by the activity of acidifying bacteria are converted into methane in two ways -by the degradation of acetic acid produced by the enzymatic activity and by low growth rate bacteria acting simultaneously with the acidifying bacteria. Trivalent chromium in the sludge does not inhibit the process, unless it is present in concentrations higher than 100 g/kg dry solids. Biomethanization reduces the volume of the 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 produced has to be purified before use.

Solid wastes 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 trimmings 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 highlighted 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 sausage casings. Collagen dispersions can be coagulated with natural and synthetic rubber latices to give low density rubber shoe soling material. Collagen can be incorporated in coating materials, in pharmaceutical applications, as an absorbant 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.

Work on alternative uses of collagen is being carried out in several countries and points to the serious concern of making practical and commercial use of chemicals, fats and protein that would otherwise be wasted through dumped trimmings, shavings and waste split. The importance of limiting protein wastage is that about 7 per cent of the weight of fresh hide is soluble protein and about 35 per cent may be lost through pre-trimming, fleshing and trimming after limed splitting.

2.3.4. **Examples of the cost of setting up effluent treatment plants**

2.3.4.1. *Industrialized countries*

Case 1

4,000 m^3 tannery + 1,000 m^3 urban, total 5,000 m^3 of effluent per day.The industrial effluent originates from tanneries processing:

	(%)
- Sole leather (veg tannage)	69
- Chrome leather (finished)	9.4
- Chrome leather (from wet blue)	14
- Leather from reptiles	5.2
- Finishing & miscellaneous	2.4

Data for 1990:
Total volume of industrial effluent treated: 906,613 m^3

Sludge produced 60,207 t

Total cost of treatment of tannery wastes (without domestic waste): approx. **US$ 12,522,400**

Cost of treatment: approx. US$ 13 per m^3

Breakdown of costs:	(%)
- Labour (36 persons)	13.9
- Electricity	3.6
- Maintenance	1.4
- Chemicals	16.1
- Sludge disposal	49.1
- Overheads,interest, etc.	13.9

Sludge handling: In 1990 the cost oscillated between US$92 and US$120 per/t of sludge (chemicals for conditioning, transport and landfill).

Only about 4 per cent of the sludge produced has been utilized in brick production at cost of approx. US$53 per/t (transport and processing).

The consortium applied the following key for charging the treatment costs according to the type of tannery:

	Cost/m^3 (US$)
A. Manufacture for third parties (vacuum drying, sammying, etc.)	4.9
B. From wet blue to finished	5.8
C. Reptile leather	6.5
D. Chrome leather	6.8
E. Vegetable sole leather	11.2
F. Finishing only	18.2

It is expected that the rates for 1991 will be changed to be based on the actual pollution load (COD and suspended solids) instead of volume.

Case 2:

Daily effluent volume 3,000 m^3

Data for 1990:

Total effluent treated	775,000 m^3
Sludge produced	15,300 t

Total cost: approx. **<u>US$ 4,836,000</u>**

Treatment cost: US$ 6.24 per m^3

Breakdown of costs:	(%)
Labour (21 persons)	21.2
Electricity	14.2
Maintenance	1.5
Chemicals	8.0
Sludge handling	36.0
Overheads, interest, etc.	19.1

Sludge disposal: the cost is identical with Case 1; they are using the same landfill. The key for cost distribution is also identical with Case 1.

Case 3

Daily effluent volume: 10,000 m^3 industrial + 3,000 m^3 total 13,000 m^3 ; different types of tanneries.

Data for 1990:

Total effuent treated	4,800,000 m^3
Industrial	3,300,000 m^3
Urban	1,500,000 m^3
Sludge produced	96,000 t

Total cost: approx. **<u>US$ 18,400,000</u>**

Average cost per m^3 of industrial effluent: US$ 5.6

Breakdown of costs:	(%)
Labour (51 persons)	13.0
Electricity	8.8
Maintenance	8.7
Chemicals	7.6
Sludge handling	54.0
Overheads, interest, etc.	7.9

Sludge disposal: same landfill and costs of Cases 1 and 2.

Tanneries are classified into seven categories as follows:

1. From raw to wet blue
2. Liming and unhairing for third parties
3. Full process (chrome)
4. From wet blue or crust to finished
5. Fleshing (there is a common treatment for these wastes)
6. Tanneries using the joint chrome recovery unit
7. Miscellaneous processes for third parties (mainly vacuum drying)

The cost is based on 60 per cent on the effluent volume and the rest is computed on the basis of pollution load (COD and suspended solids). The rates vary from US2.2m^3$ (category 7) to US$ 7.8 m^3 (category 2).

It is estimated that in Case 1 water consumption in tanneries has gone down to about 12 to 15 l/kg of raw material; estimating that in 1990 the cluster may have processed about 60,000 t of hides. It could be very roughly estimated that the cost of effluent treatment was approx. US$ 0.20 dollars per kg of processed hide, ie US$ 200 per t. Capital and operation costs of treatment at some tanneries in the USA are shown in table 12.

2.3.4.2. *Developing countries (Africa)*

Tannery 1

i) Daily input 6 t of wet salted hides processing 80 per cent up to wet blue stage, 20 per cent fully finished leather, effluent volume 250 m^3, located outside residential area, on the river bank (high dilution)

ii) Separate chrome treatment, lime liquors buffer tank, lifting tank, two brushed screens, equalization-cum-sulphide oxidation tank with two Venturi ejectors, dosing pumps for manganese alum and polyelectrolite, settling, sludge pumps, sludge drying beds, a simple system of facultative lagoons; basic monitoring equipment

iii) Equipment including plant design, assembling, installation and commissioning:

	US$
approx.	200,000
Civil works	140,000
Total:	340,000

Tannery 2

i) Daily input 5,000 dry skins processed up to wet blue, daily effluent volume 200 m^3 within urban area, on the river bank with low flow

ii) Separate chrome treatment (precipitation), mixer, screening, lifting (two submersible pumps) equalization with sulphide oxidation with two injectors, dosing pump, alum coagulation, three sludge pumps, one surface aeratom, settling, aerated lagoon, sludge drying beds

iii) Equipment including plant design, assembling, installation and commissioning:

	US$
approx.	120,000
Civil works	50,000
Total:	170,000

Tannery 3
(Up-grading of the existing treatment plant)

i) Daily input 3 t of wet salted hides,processing to wet blue, daily effluent volume 120 m^3,located in the industrial zone, connected to the industrial sewerage system

ii) Separation of chrome (precipitation), bar screening, equlization-cum oxidation with air blower and diffusers, sedimentation, aerated lagoon, polishing lagoon, sludge pumps, sludge drying beds

iii) Equipment including plant design, assembling, installation and commissioning:

	US$
approx.	60,000
Civil works	35,000
Total:	95,000

Tannery 4

i) Daily input 1,500 wet salted hides and 4,500 skins,approx 60 per cent semi-processed (pickled, wet blue) the rest fully finished, daily effluent volume 2,000m^3, located in the industrial zone, connected to the sewerage system

ii) Brush screening, lifting tank, equlization-cum-oxidation, alum coagulation, settling, sludge thickening, belt press

iii) Equipment including plant design, assembling, installation and commissioning:

	US$
approx.	1,400,000
Civil works	1,000,000
Total:	2,400,000

3. BARRIERS TO ACHIEVING ESID

3.1. TECHNICAL CONSIDERATIONS

By nature, tanners are very conservative. This is not simply an obstinacy against change, it is because the quality and character of leather is prone to change when the parameters of processing are altered. **Changes in the length of processes, process temperatures, float volumes, uptake of chemicals etc. influence the ultimate character of the leather.** Leather being produced from a complex, non-uniform natural protein material still requires considerable craft in its manufacture. The adoption of low waste technology often requires a radical alteration of most tannery processes while, at the same time, ensuring that the ultimate product retains its marketable properties. Therefore if a tanner is producing consistent quality of leather which satisfies his customers using a process which may be wasteful in water, energy and chemical utilization, he may resist altering his operations to comply with environmental demands.

The problem of introducing low waste technology is common to the industry in both developed and developing countries.

Traditionally, in most developing countries tanning operations are a **family business**, carried out in **small to medium scale semi-mechanized units**, very frequently grouped tightly **in clusters** which used to be outside residential areas. Tanners in such units have no formal education and have little or no understanding of the complexities of the leather processing, their skills acquired from their elders with **hardly any perception of environmental protection.**

Most of the major leather and footwear producing developed and developing countries have research and development laboratories and technological teaching facilities. In some cases an economic grouping of countries will share such facilities. It is usual that either the R & D laboratories or the teaching establishments, or both, have pilot tanneries in which technological developments are taken a stage further towards commercial leather production by industry. Some of these have pilot effluent treatment facilities which are of benefit in helping the local industry adopt relevant methods of emission limitation and treatment. An example of this is the effluent treatment plant installed some years ago at the Brazilian Tanners School at Estancia Velha (RS) with UNIDO assistance.

Nevertheless **there remains a problem in transferring technology from laboratory and pilot plant of an R & D to practical everyday use in the industry.**

Technical assistance laboratories must be as concerned with maintaining leather characteristics as with reducing pollution load and they must also work with tanners in their factories to achieve these objectives, rather than in the isolation of R & D establishments.

Low waste technologies, generally speaking, **require better skilled personnel and closer technical control than conventional processing.** Thus, **the lack of properly trained staff at different levels remains one of the crucial constraints.**

Even in the most advanced developing countries **there is a lack of up-to-date knowledge of and practical experience in design, installation and efficient operation of tannery wastewater treatment plants;** this lack of expertise is seen particularly in the case of common effluent treatment plant facilities for tannery clusters.

3.2. ECONOMIC CONSIDERATIONS

<u>The cost of introducing a cleaner processing method may be prohibitive and beyond the reach of a small scale tanner;</u> the price of the special drum for hair save unhairing with the necessary auxiliary equipment may be as much as twice of the conventional drum. Enzyme unhairing needs very accurate control and consistency of all parameters (pH, temperature,float etc) which is possible to achieve only in rather sophisticated tanneries and is associated with higher production costs (partly off-set by lower wastewater treatment expenses). High chrome exhaustion tanning requires very expensive specialty chemicals, normally proprietary products.

In the industrialized countries the leather industry has had to suffer economic constraints but these are not as onerous as in developing countries. Interest rates on borrowed capital are frequently much higher. As the industry has advanced to greater production of finished leather, the amount of capital tied up in work-in-progress has increased along with the necessity to keep higher inventories of chemicals, machinery spares, etc. Because of problems with poor infrastructure in many developing countries, the tanneries have always kept higher stocks of chemicals than their counterparts in developed countries, against the contingency of delays in delivery from ports. Another disadvantage is the imposition of import duties on chemicals and machinery. Few specialty chemicals for tanning are produced in developing countries, although basic chemicals such as salt, lime, sulphuric acid, sodium sulphate or sodium carbonate may be available indigenously. Most tanning materials, dyes, fat liquors, special auxiliaries and finishes need to be imported. Duties depend on government policy and they can range from zero to over 100 per cent.

Cost of plant and chemicals for treating effluent can be another heavy cost. While tanners in developing countries may be shielded from the perils of raw material market fluctuations through market protection policies and while they may benefit from fiscal incentives in their operation, tanners in developed countries do not need to carry high inventories nor do they suffer the often inordinately high cost of capital or the inflation rates of many developing countries.

Thus relative advantages in the various locii of manufacturing may balance out. Tanners in developed countries have either invested in effluent treatment or opted to concentrate on processing semi-processed material purchased domestically or from abroad. Translated into dollars per square foot the on-cost of effluent treatment in 1987 in the following countries was:-

Hungary	2.8 - 3.5 cents per ft^2 [1]
Italy	7.7 - 10.3 cents per ft^2

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[1] (1 ft = 9.29 cm^2)

U.K.	8.3 - 10.0 cents per ft^2
Germany	8.1 - 10.0 cents per ft^2

Initial treatment costs may not result in this level of on-cost in developing countries, but as standards become more stringent they will inevitably increase. Such additional cost could tip the economic balance in favour of processing in developed countries. In fact some developing countries already import wet blue and crust leathers from specially developed plants in developed countries.

3.3. INADEQUATE LEGISLATION AND LACK OF MONITORING FACILITIES

Pollutant discharge standards in most developing countries **are by nature rigid and have a disregard for specific site conditions. Instead of a gradual approach as** called for which would phase installation of treatment facilities (for example the physico-chemical first followed by the biological treatment and appropriate sludge handling) **a tanner is under pressure to put up a complete treatment system and meet all discharge limitations at once** which is beyond his financial and technical means.

In addition to the regular process and quality control tannery laboratories must be able to measure the following specific pollution parameters: pH, suspended solids, total dissolved solids, sulphide, ammonia nitrogen, chromium, aluminium, phenols, VOCs and CODs (COD and conduct a jar test); larger plants should also be able to measure the biochemical oxygen demand (BOD_5) and thus establish the ratio of COD to BOD_5 which can be used as an indicator of biodegradability.

However, very few tanners have the necessary process and effluent treatment control facilities and legislation enforcement agencies usually lack skilled personnel to monitor performance of the installed treatment plants.

Thus **the means for proper enforcement are essential.** If legal enforcement of the standards is not put into effect, it is understandable that the required environmental standards may not be observed.

As a very general guideline for a medium scale tannery discharging effluents into an open recipient (middle flow river) the following standards could be suggested:

Temperature	25-35°C maximum
pH value	6.0-9.0
Settling substances	0.5 mg
Non-biologically degradable substances (extracted by petroleum ether)	20 mg
Cr VI	0.1-0.5 mg
Cr III	2.0 mg
Sulphides	2.0 mg
Sulphates	400 mg SO_4
Free phenols	20 mg
Ammonia nitrogen	50 mg
BOD_5	100 mg
COD	200 mg

3.4. SOCIAL CONSIDERATIONS

Tanning is a traditional industry. In many developing countries it is carried out by a certain sector of society. Simply tanned leathers are produced for local craftsmen to manufacture into leather products for local markets. Methods of tanning and fabrication of goods are far removed from modern methods. Such segments of society are difficult to bring within the modern framework of production and emission control. Governments often feel inhibited from dealing with such problems because of the social and even political upheaval that would occur. The problem is further exacerbated in India and Japan where tanners are traditionally regarded as socially inferior because of the nature of their work. These groups, because of traditional discrimination, have amassed considerable political privileges. Consequently there are difficulties in altering the structure of artisan industry.

Industrialized tanners in some developing countries who face the enforcement of emission regulations are in some instances contracting their wet work processing to artisan tanners who continue to operate without restrictions.

3.5. GRADUAL PROGRESS

Tanners in developing countries can begin by adopting good housekeeping measures which require little or no capital investment, such as water conservation at all stages of wet processing. Savings in chemicals by introducing reuse-recovery-recycle systems can pay for the simple equipment needed to run them, such as collection pits, pipes and pumps. Tanners in developing countries can reduce the pollution load by pursuing 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 wastes; investigating the feasibility of extracting methane, saving hair for conversion into felt; turning waste split and untanned trimmings into gelatine, protein powders and collagen for sausage casings and medical and surgical films; turning fleshings into glue, animal feed protein and fertilizers and tanned waste into leatherboard, filter media, non-wovens and other end uses. By commercializing solid wastes, the cost of effluent treatment can, to some extent, be covered.

4. INDUSTRY, GOVERNMENTS AND INTERNATIONAL CO-OPERATION

4.1. ENVIRONMENTAL LOBBY

The leather industry in many countries has responded positively to the environmental problem. There has been an awareness that environmental safety legislation would inevitably enforce stricter controls. For the future the search proceeds for tanning materials that can realistically replace chromium, unhairing systems that are efficient and do *not* rely on sulphides, deliming methods that do not require ammonium salts and vast reductions in emission of VOCs through elimination of solvents in fishing.

The governments lobby of legislature is increasing in its intensity. Governments are developing regulatory frameworks to protect public health. During the last twenty years in the USA there have been a number of acts which have tightened environmental safety rules. Realistic scientifically based objectives should be instituted rather than unattainable standards resulting from political or even emotional motivation. Good co-operation between the industry and governments is therefore essential.

A rather good overview of the possible thrust of actions to be taken by the industry can be gained from the conclusions and recommendations of two meetings organized by UNIDO on pollution control in the tanning industry.

A) Country participants from China, India, Indonesia, Pakistan, Sri Lanka and Thailand supported by a team of high-level international consultants at the UNIDO Expert Group Meeting on Pollution Control in the Tanning Industry in the South-East Asia Region, held in Madras, India, from 15 to 17 February 1991, under the project US/RAS/89/246 referred to above, identified the following areas as of common interest to them:

i) Need for a pollution control awareness campaign to implement environmentally friendly technologies and co-ordinate activities to introduce specific measures facilitating the introduction and implementation of low waste technologies in the leather sector.

ii) Demonstration effluent treatment plants for individual tanneries and clusters of tanneries, together with necessary laboratory monitoring facilities.

iii) Innovative schemes to promote relocation of tanneries for improving the environmental situation.

iv) Development of internal design capabilities.

v) Special training programmes for operating personnel for effluent treatment plants.

vi) Integrated approach for pollution control and waste management, including chrome recycling and/or recovery and sludge handling and disposal.

They further identified the following areas which should be given priority.

(a) **Tanning industry needs qualitative boost in developing countries**

Despite the economic importance of the leather industries for the economies of developing countries there is a discriminating attitude towards them because of the high pollution level. The younger generation at colleges and technical institutions do not find the tanning industry very attractive and are likely to select other industrial options.

Developing countries should work towards a qualitative up-grading of the tanning industries. New industrial complexes should be designed, on a modern basis, incorporating all possible equipment safeguards and intrinsic safety features, to house new tannery units and relocate those currently beset with serious pollution problems.

(b) **The technology transfer mechanism** is weak in the implementation of new concepts in environmental pollution control involving in-process, end of pipe and reuse/recycle measures in the leather industry.

UNIDO could assume a catalytic role in providing experts/consultants and services of project engineering firms in implementing new projects in developing countries, preferably through horizontal transfer of technology routes. Know-how and design engineering packages have to be developed on commercial lines by involving know-how and project engineering firms from the more industrially advanced developing countries. Support from UNIDO/UNDP by providing necessary funding for this activity will go a long way towards strengthening the design engineering base.

It may be noted that some of the process know-how for tannery by-product utilization, slaughter house by-product utilization and end of pollution control measures are available in some of the developing countries. If necessary means are provided, they can be transferred to other developing countries.

(c) **Human Resource Development**

This is an important area for UNIDO's consideration. Most of the developing countries are facing acute shortage of technically qualified personnel for the operation, monitoring and maintenance of effluent treatment plants for tannery wastes. Appropriate training and education programmes are needed to cater for the needs of technical personnel at various levels (operating, supervisory, managerial and design). There is a urgent need to prepare a working paper which precisely identifies a training curriculum, type of faculty and infrastructural facilities required for this purpose. The existing expertise and facilities available in some of the developing countries should be taken into consideration and if necessary they should be strengthened and made more broad-based to cater for the regional needs.

(d) **Setting up demonstration plants on commercial level needs urgent consideration**

Pollution control technologies have to be techno-economically viable with attractive financial returns for adoption in the traditional leather sector. The technology packages should consist of in-plant control, end of the pipe treatment and waste management components. There is a great need to set up demonstration plants for common effluent treatment, in-plant process controls and tannery waste utilization in the midst of tanneries in selected developing countries in order to enable them to see the performance of the new systems under field conditions. The demonstration plants should also be utilized for training of technical personnel from the developing countries. Adequate attention should be paid to the management of the demonstration plants. Sharing of managerial responsibilities by the existing tanneries will promote the cause of smooth technology transfer and generate a multiplier effect.

B) Conclusions and Recommendations of the UNIDO/UNDP Workshop on Pollution Control/ Low-Waste Technologies in Agro-based Industries in Selected Countries from the Asia and the Pacific Region held in Shanghai, China, 24-28 September 1990

For the Leather Industry:

The beamhouse (unhairing) and the tanyard, the two main sources of pollution in a tannery, should be the first to be considered for introduction to cleaner technologies in leather processing; utilization of chrome-free solids as by-products and disposal of chrome containing sludge are possibly the issues that require particular attention.

In preservation of raw hides and skins use of excessive quantities of salt as well as utilization of harmful biocides should be avoided. Where feasible fresh hides and skins are to be taken for processing.

Conventional tanneries should be expected to tighten-up on the accuracy of their operations to prevent wasting resources, chemicals and water and to avoid these becoming sources of pollution; introduction of modern production control systems should be encouraged.

There is already a wide range of low-waste processing options available to the tanner: green fleshing, hair-saving beamhouse systems, ammonium-free deliming, high chrome exhausting and/or chrome-free tannages, organic-solvent free finishing, etc., including recycling of floats and chrome recovery. Such systems should be greatly promoted.

Considerable amount of wastes in a conventional tannery can be seen as valuable by-products which can be converted into saleable products like gelatine, glue, fodder, fertilizer, etc.

A phased approach to installing effluent treatment plants, i.e. physico-chemical (primary) followed by biological (secondary) treatment optimized on the basis of actual performance of the primary system is considered advantageous.

Joint effluent treatment plants are very often the best solution for tannery clusters (as a rule consisting of small and medium-scale type units) so typical for this region; combined with domestic waste they offer technical advantages with an economy of scale. However, in view of the lack of experience in designing and operating such systems, the installation of demonstration plants, preferably on an industrial scale, is very much needed.

Information and training programmes have to facilitate a better understanding of the linkage between production and treatment, monitoring of equipment in the case of breakdowns and the changes of effluent composition as well as handling of hazardous chemicals and by-products.

Local authorities concerned have to provide suitable landfills for safe disposal of chrome containing solid wastes.

4.2. THE NEED FOR AN ENVIRONMENTAL DATABASE

The need for an easily accessible source of information on clean technologies inspired the British Leather Confederation, which provides the Secretariat for the International Union of Leather Technologists and Chemists' Environment and Waste Commission to gather information in co-operation with six other leather research institutes. The work is dependent upon the development of a network of co-operation and support, involving tanners, industrial research centres, industry suppliers, the Government and other agencies (e.g. the European Commission under the SPRINT programme, the United Nations Environment Programme etc.) and independent leather experts. Tanners through their trade or R & D associations in developing countries would be wise to become involved with this programme.

The main objective is to set up a practically useful system to enable the tanner to easily shortlist appropriate technologies for his requirements from the database. For the practising tanner there is a world of difference between results claimed by an R & D centre or a chemical supplier *and* what happens in reality. Not only may the technology be suspect, but differences in the costs of chemicals and/or energy can have a significant impact on process economies in different countries. This aspect is particularly relevant as regulatory agencies, or consultants working for them frequently scour the technical literature without ascertaining the true status of the technology they may be imposing.

As part of this procedure, it is also essential for the tanner to be able to identify existing users of the technology and independent leather experts, as well as the manufacturers or inventors, whom the tanner can then separately consult. It is considered most important that the database should not just be a bibliographic source of information but should be of immediate practical use, quantifying, wherever possible, the reductions in pollution achievable by the clean technology, listing any disadvantages and, above all, giving an indication of its present level of development and extent of use, since systems inevitably range from those just at the research and development stage to well established technologies in widespread use.

4.3. GOVERNMENT INVOLVEMENT IN POLLUTION REDUCTION

4.3.1. **Indian government helps industry**

It is estimated that nearly 70 per cent of all hides in India are tanned in Tamil Nadu. In early 1990, to break the deadlock in setting up effluent treatment plants in the state of Tamil Nadu, the Indian Government made a plan to provide 25 per cent of the cost of establishing common treatment facilities at six centres. Additionally, the state of Tamil Nadu is providing 25 per cent, tanners are expected to pay 15 to 20 per cent and the remainder will be made up of loans from financial institutions. The cost of maintaining the effluent treatment facilities once they are operating will be the responsibility of the tanners.

Meanwhile in the north of India, as part of the massive action plan to cleanse the river Ganges in North India of sewage and industrial wastes, India's Central Leather Research Institute has been associated with the National Environmental Engineering Research Institute in setting up tannery effluent treatment facilities for the Kanpur tanneries.

The project has involved the design and installation of a chrome recovery plant in a commercial tannery. The full scale demonstration plant has 125 cubic metres per day capacity. The Netherlands Government through the Dutch leather research organisation (TNO) is associated with the Ganges cleansing plan.

Co-operation between government and industry and involvement of R & D organisations from developed countries in environmental projects carried out in developing countries such as outlined in India could be evolved in many countries, given the willingness for co-operation between industry and governments and financial help and incentives from the Government.

4.4. ACTIVITIES OF UNIDO

During the last few years pollution control has taken a very prominent role in UNIDO technical assistance to the leather and leather products industry so that at present there is virtually no project in the tanning sector without an environmental component.

As a rule, cleaner and low waste technology and end-of-pipe treatment issues are simultaneously addressed. Advice in defining, monitoring and enforcement of emission standards is also given as required.

Assistance is extended both to individual industrial plants or agglomerations of tanneries and to leather R & D establishments. As a matter of policy, any assistance to leather R & D and training centres includes installation of a pilot and demonstration plant for treatment of tannery wastes as until recently none of the centres in developing countries had such facilities. They are encouraged to expand pollution control component in their training programmes and strengthen their capabilities in designing tannery effluent treatment plants.

Dissemination of information on environmental protection is another important area of UNIDO activities in the leather sector: the Latin American Seminar on Treatment of Tannery Wastes was held in Porto Alegre, Brazil, in 1987; UNDP/UNIDO Workshop on Pollution Control/Low Waste Technologies in the Agro-Based Industries for the Asia and Pacific Region in Shangahai, China, in 1990; Expert Group Meeting on Pollution Control in the Tanning Industry in the Region of South-East Asia, Madras, India in February 1991, as well as other numerous short courses, open weeks, round table conferences etc held in Indonesia, Kenya, Costa Rica, Pakistan and other countries. A considerable amount of background material, a number of studies and reports on cleaner technology and treatment of wastes have been prepared and distributed, one of the latest being UNEP/UNIDO technical guide, Tannery and Environment.

The **pilot and demonstration plant** designed, installed and operated with UNIDO assistance at the Tanning School at Estancia Velha, RG, is possibly unique of that kind throughout the world. Effluents from the school tanning unit and the nearby tannery are used to conduct trials for which a wide range of physico-chemical and biological treatment systems are at their disposal, i.e. from chrome recycling, screening, catalytic oxidation of sulphide, homogenization with aeration by diffused air or surface aerators, coagulation and flocculation to several parallel biological treatments: oxidation ditch, facultative aerated lagoon, high load activated sludge and a trickling filter. A thickener, sludge drying beds, a flotation and an ultrafiltration unit and a fully equipped laboratory have also been installed. A comprehensive training programme for counterparts has been presented.

Under UNIDO projects of technical assistance a number of industrial scale tannery effluent treatment plants have been installed in Burundi, Malawi and Mozambique. Within the sectoral programme for Africa designs have been made and equipment ordered for wastewater treatment for three wet blue tanneries (Kenya, Tanzania, Zambia) to be put into operation before end of 1991. These plants are intended to serve as kind of " models " for other tanneries in the region. Outline of treatment systems was made for about 100 tanneries in Brazil. A design for a unit in Katmanu, Nepal, was prepared but not implemented.

A design of the mixed trade and domestic waste treatment system combined with a socio-economic study is under preparation for the tannery cluster in Kasur, Pakistan and funds have been secured for design and part of equipment for a similar plant in the state of Tamil Nadu, India.

Advice is being given to national experts in improving the performance of large scale plants in Shanghai, China, and Franca, the Sao Paolo State, Brazil.

Pilot plants with laboratories annexed to leather development centres are already operational (KIRDI, Nairobi) or under construction (CETEC, San Jose, Costa Rica; LIRC, Hanoi, Viet Nam). A pollution control laboratory with well trained staff has been established at IRDLAI, Yogyakarta, Indonesia.

The treatment of tannery effluents in South East Asia is under preparatory assistance. UNIDO consultants have visited Bangladesh, China, India, Indonesia, Nepal, Pakistan, Sri Lanka and Thailand, in order to assess the levels or environmental degradation caused by the tanning industry in each country. Their findings and recommendations were reviewed in the Expert Group Meeting in Madras. Subsequently a very comprehensive <u>sectoral programme covering a wide range of problems from introduction of environmentally friendly technologies, in-plant training and training in industrialized countries, setting up laboratories and pilot and demonstration plants, installation of waste water treatment plants for clusters of small and medium scale tanneries, disposal of solid wastes, utilization of by-products etc are addressed. The programme calls for UNIDO inputs of over 14 million dollars and is ready for submission to potential donor countries</u>.

(A significant part of UNIDO on-going pollution control activities in the tanning industry is funded through Special Purpose Contribution by several donor countries).

5. CONCLUSIONS

5.1. BARRIERS TO PROGRESS

The main barriers to the adoption of more environmentally acceptable methods of leather processing and effluent treatment are:-

(a) The cost of specialty chemicals required in reducing or eliminating the use of the main polluting chemicals;

(b) The cost of purchase and installation of water conservation devices, waste water collection and reuse equipment;

(c) The cost of effluent treatment chemicals and equipment;

(d) The cost of physical, chemical and biological process and effluent monitoring equipment;

(e) The training and added personnel cost of maintaining technical control of low waste technologies and effluent treatment;

(f) Traditional conservatism in the industry which derives from hesitation over process alterations if satisfactory leather is being produced;

(g) The frequent remoteness of government-backed R & D facilities from the everyday practicalities of leather-making;

(h) Social constraints emanating from traditional tanner groups where resistance to change is compounded by political influence;

However, stricter environmental legislation will inevitably be enforced in all developing countries sooner or later. Therefore environmental auditing, promotion of cleaner technologies and the establishment of appropriate effluent treatment plants are increasingly essential.

5.2. EVALUATION OF POLLUTION CONTROL REQUIREMENTS

(a) Investigation into causes of pollution should be carried out before detailed solutions are devised. A large number of assessment, auditing and evaluation methods are available for governments and industry through U.N. agencies.

(b) Good housekeeping' and improved process optimization should be carried out before new technology is considered. In some conventional tanneries possibly over 50 per cent of pollution can be eliminated by combination of good houskeeping and process control and very simple wastewater treatment at marginal cost.

(c) Chemical safety in the workplace and in the public domain should be observed during operations in all plants.

(d) Avoiding waste is the first priority followed by waste recovery and re-use. Treatment and disposal is the final option for residuals that cannot be avoided.

(e) Waste treatment and disposal must be carried out to avoid secondary environmental problems arising from such treatment (such as disposal of solid wastes).

(f) Effective motivation and clear responsibility is essential if pollution control staff are to carry out their jobs.

5.3. CLEANER TECHNOLOGIES

The two main sources of pollution in a tannery are unhairing and tanning. These should be the first places to consider introducing cleaner leather processing technologies. See figure V.

Conventional tanneries should try to prevent wasting resources, chemicals and water which become sources or pollution. The introduction of modern production control systems should be encouraged.

Excessive quantities of salt and harmful biocides should be avoided when preserving raw hides and skins. Fresh hides and skins should be taken for processing where possible.

A wide range of low waste processing methods are available to the tanner and should be promoted. These include green fleshing, hair saving beamhouse systems, ammonium-free deliming, high chrome exhausting and/or chrome-free tannages, organic solvent free finishing, including recycling of floats and chrome recovery.

Many tannery wastes are valuable by-products which can be converted into saleable products like gelatin, glue fodder and fertilizer.

5.4. EFFLUENT TREATMENT

There should be a phased approach to installing effluent treatment plants, for example physico-chemical (primary) followed by the biological (secondary) treatment optimised on the basis of actual performance of the primary system.

Joint effluent treatment plants are often the best solution for tanneries that are grouped in zones (usually consisting of small and medium scale type units). When combined with domestic waste they offer technical advantages and have an economy of scale.

Information and training programmes need to give better understanding of the link between product and treatment, monitoring of equipment in the case of breakdowns and the changes of effluent composition, as well as handling of hazardous chemicals and by-products.

Local authorities need to provide suitable landfill sites for the safe disposal of chrome-containing solid wastes.

5.5. UNIDO's ROLE

UNIDO's position is very specific as it has the competence and has accumulated considerable experience in dealing with both reducing the pollution at its very source (introduction of low waste technology) and with treatment of wastes (end-of-pipe) according to methods suitable for conditions prevailing in developing countries.

TABLE 1. HIDES, SKINS AND LEATHER FOOTWEAR: THEIR SIGNIFICANCE IN RELATION TO TRADE IN OTHER COMMODITIES (1985 to 1987)

	DEVELOPING COUNTRIES	DEVELOPED COUNTRIES	WORLD
	(........ Million US Dollars ....)		
HIDES AND SKINS			
RAW HIDES AND SKINS FROM BOVINE, SHEEP AND GOAT	399.0	3 455.5	3 854.5
LEATHER (Rough-tanned and finished, all types)	1 510.1	3 250.5	4 760.6
FOOTWEAR WITH LEATHER UPPERS	3 524.0	8 533.0	12 057.0
TOTAL ABOVE	5 433.1	15 239.0	20 672.1
MEAT			
MEAT FROM BOVINE, SHEEP AND GOATS	2 582.7	11 702.3	14 285.0
CANNED AND PREPARED MEAT (All Types)	761.9	3 169.4	3 931.3
TOTAL ABOVE	3 344.6	14 871.7	18 216.3
SELECTED OTHER COMMODITIES			
RUBBER	3 095.7	78.7	3 174.4
COTTON	2 991.7	3 020.3	6 012.0
COFFEE	11 096.6	580.7	11 677.3
TEA	1 779.3	-	1 779.3
RICE	1 839.0	1 333.0	3 172.0
TOBACCO	1 721.7	2 244.3	3 966.0

Source: The Food and Agriculture Organization of the United Nations

TABLE 2. RAW HIDES AND SKINS: FACTORS DETERMINING LEVEL OF OUTPUT (1985-87)

	BOVINE HIDES AND SKINS INCLUDING BUFFALOES					SHEEP AND LAMBSKINS					GOAT AND KIDSKINS				
	Live-stock Popu-lation	Share of global herd	Ratio of output to live-stock numbers	Numeri-cal output	Average unit weights	Live-stock Popu-lation	Share of global herd	Ratio of output to live-stock numbers	Numeri-cal output	Average unit weights	Live-stock Popu-lation	Share of global herd	Ratio of output to live-stock numbers	Numeri-cal output	Average unit weights
	Mill. head	Percent		Mill. pieces	Kg wet salted	Mill. head	Percent		Mill. pieces	Kg dry without wool	Mill. head	Percent		Mill. pieces	Kg dry
WORLD	1 409.7	100.0	19.6	276.0	17.85	1 138.8	100.0	41.0	467.0	0.80	493.6	100.0	40.7	200.7	0.71
DEVELOPING COUNTRIES 1/	992.0	70.4	12.8	127.4	14.69	600.6	52.7	37.9	227.5	0.62	465.2	94.2	39.9	185.5	0.71
LATIN AMERICA	310.3	22.0	13.4	41.5	19.68	113.7	10.0	22.0	25.0	0.81	33.5	6.8	35.8	12.0	0.61
AFRICA	142.9	10.2	10.1	14.4	13.23	138.5	12.2	29.5	40.9	0.70	139.3	28.2	31.1	43.3	0.56
NEAR EAST	56.4	4.0	22.3	12.6	14.95	150.9	13.2	57.4	86.6	0.60	57.3	11.6	43.5	24.9	0.73
ASIA & THE PACIFIC	383.4	27.2	13.4	51.5	10.78	87.7	7.7	44.2	38.8	0.59	165.7	33.6	44.8	74.2	0.86
ASIAN CENTRALLY PLANNED 2/	98.6	7.0	7.5	7.4	16.06	109.8	9.6	33.0	36.2	0.50	69.3	14.0	44.9	31.1	0.60
DEVELOPED COUNTRIES	417.7	29.6	35.6	148.6	20.56	538.2	47.3	44.5	239.5	0.96	28.4	5.8	53.5	15.2	0.72
NORTH AMERICA	117.6	8.3	37.6	44.2	23.84	11.0	1.0	56.4	6.2	0.89	1.7	0.4	47.1	0.8	0.99
WESTERN EUROPE	97.6	6.9	38.9	38.0	23.66	96.2	8.5	71.1	68.4	0.89	11.0	2.2	71.8	7.9	0.54
EASTERN EUROPE & USSR	154.7	11.0	33.4	51.6	15.72	182.9	16.1	43.4	79.3	0.72	8.5	1.7	43.5	3.7	0.91
OCEANIA	30.9	2.2	33.7	10.4	18.24	218.0	19.1	35.0	76.2	1.29	1.2	0.3	66.7	0.8	0.97
OTHER DEVELOPED	16.9	1.2	26.0	4.4	23.10	30.1	2.6	31.2	9.4	1.00	6.0	1.2	33.3	2.0	0.80

1/ Figure shown may be slightly different from sum total due to existence of some "other developing countries" not shown separately.

2/ Including Taiwan Province of China.

Source: FAO World Statistical Compendium for Raw Hides and Skins, Leather and Leather Footwear, 1989.

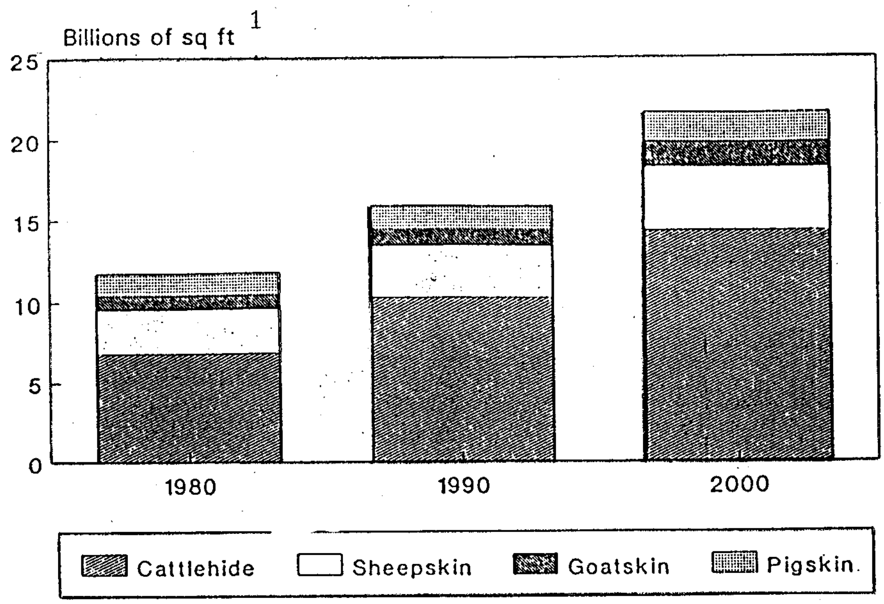
TABLE 3. LEATHER: DEVELOPMENTS IN OUTPUT BY TYPE AND ECONOMIC ZONE

	HEAVY LEATHER				LIGHT LEATHER FROM BOVINE ANIMALS				LIGHT LEATHER FROM SHEEP & GOATS			
	Average		Growth	Share of world output	Average		Growth	Share of world output	Average		Growth	Share of world output
	1961-65	1985-87		1985-87	1961-65	1985-87		1985-87	1961-65	1985-87		1985-87
	'000 tons		Percent		Million Sq. Ft.		Percent		Million Sq. Ft.		Percent	
WORLD	564.4	453.2	- 19.7	100.0	5 152.0	8 878.5	72.3	100.0	2 416.1	3 313.5	37.1	100.0
DEVELOPING COUNTRIES	121.5	186.8	53.7	41.2	1 664.3	4 004.9	140.6	45.1	623.5	1 564.9	151.0	47.2
LATIN AMERICA	51.2	57.5	12.3	12.7	530.7	1 564.4	194.8	17.6	70.6	183.1	159.3	5.5
AFRICA	1.9	3.0	57.9	0.7	69.8	201.4	188.5	2.3	60.6	217.9	259.6	6.6
NEAR EAST	13.2	21.7	64.4	4.8	135.6	298.2	119.9	3.4	93.2	330.2	254.3	10.0
ASIA & THE PACIFIC	24.0	75.8	215.8	16.7	691.2	1 601.8	131.7	18.0	297.1	629.3	111.8	19.0
ASIAN CENTRALLY PLANNED 1/	31.1	28.8	- 7.4	6.3	237.0	339.1	43.1	3.8	102.0	204.4	100.4	6.1
DEVELOPED COUNTRIES	442.9	266.4	- 39.8	58.8	3 487.7	4 873.6	39.7	54.9	1 792.6	1 748.6	- 2.5	52.8
NORTH AMERICA	89.4	25.0	- 72.0	5.5	906.0	712.0	- 21.4	8.0	221.5	59.9	- 73.0	1.8
WESTERN EUROPE	126.2	65.5	- 48.1	14.5	1 509.0	2 379.3	57.7	26.8	1 005.2	1 195.1	18.9	36.1
EASTERN EUROPE & USSR	197.7	145.7	- 26.3	32.1	743.4	1 448.5	94.8	16.3	534.9	413.1	- 22.8	12.5
OCEANIA	11.0	19.8	80.0	4.4	87.2	57.1	- 34.5	0.7	6.2	33.5	440.3	1.0
OTHER DEVELOPED	18.6	10.4	- 44.1	2.3	242.1	276.7	14.3	3.1	24.8	47.0	89.5	1.4

1/ Including Taiwan Province of China.

Source: FAO.

TABLE 4. WORLD LEATHER SUPPLY BY RAWSTOCK
1980, 1990 AND 2000



[1]/ 1 $ft^2 = 9.29\ dm^2$

TABLE 5. FOOTWEAR WITH LEATHER UPPERS: DEVELOPMENTS IN PRODUCTION, TRADE AND AVAILABILITY BY ECONOMIC ZONE

	PRODUCTION				EXPORTS				APPARENT CONSUMPTION			
	Average		Growth	Share in world output	Average		Growth per annum	Share in world output	Total Average		Per Caput Average	
	1961-65	1985-87		1985-87	1961-65	1985-87		1985-87	1961-65	1985-87	1961-65	1985-87
	Million Pairs		Percent		Million Pairs		Percent		Million Pairs		Pairs	
WORLD	2 449.1	3 864.9	57.8	100.0	135.9	1 065.1	9.4	100.0	2 444.2	3 846.3	0.8	0.8
DEVELOPING COUNTRIES	539.8	1 527.9	183.0	39.5	11.5	435.1	17.1	40.9	540.7	1 124.3	0.2	0.3
LATIN AMERICA	177.4	462.2	160.5	12.0	2.0	137.6	20.0	12.9	178.2	329.8	0.8	0.8
AFRICA	18.5	63.0	240.5	1.6	1.2	5.0	6.4	0.5	23.8	62.0	0.1	0.1
NEAR EAST	67.6	187.6	177.5	4.8	0.1	4.6	18.1	0.4	68.0	189.8	0.5	0.8
ASIA & THE PACIFIC	177.6	572.2	222.2	14.8	5.2	187.7	16.9	17.7	175.0	399.7	0.2	0.3
ASIAN CENTRALLY PLANNED 1/	98.7	242.9	146.1	6.3	3.0	100.2	16.5	9.4	95.7	143.0	0.1	0.1
DEVELOPED COUNTRIES	1 909.3	2 337.0	22.4	60.5	124.4	630.0	7.3	59.1	1 903.5	2 722.0	1.9	2.2
NORTH AMERICA	558.1	250.8	- 55.1	6.5	2.8	3.6	1.1	0.3	583.6	720.1	2.8	2.7
WESTERN EUROPE	625.5	881.5	40.9	22.8	87.1	535.9	8.2	50.3	594.8	782.3	1.8	2.1
EASTERN EUROPE & USSR	638.6	1 094.7	71.4	28.3	33.4	89.2	4.4	8.4	637.5	1 101.3	2.0	2.8
OCEANIA	33.2	22.0	- 33.7	0.6	-	0.3	-	-	34.4	25.6	2.6	1.3
OTHER DEVELOPED	53.9	88.0	63.3	2.3	1.1	1.0	- 0.5	0.1	53.2	92.7	0.5	0.6

1/ Including Taiwan Province of China.

Source: FAO.

TABLE 6. COMPOSITION OF TYPICAL UNTREATED COMBINED TANNERY EFFLUENT (Units are mg/l unless otherwise indicated)

Parameter (mg/l)	Chrome Tannage	Vegetable Tannage
pH	9	9
Total solids	10 000	10 000
Total ash	6000	6000
Suspended solids	2500	1500
Ash in suspended solids	1000	500
Settled solids (2 h)	100	50
BOD_5	900	1700
$KMnO_4$ - value	1000	2500
COD ($K_2Cr_2O_7$)	2500	3000
Sulphide	160	160
Total nitrogen	120	120
Ammonia nitrogen	70	70
Chrome (Cr)	70	-
Chloride (Cl^-)	2500	2500
Sulphate (SO_4)	2000	2000
Phosphorus (P)	1	1
Ether extractable	200	200

Source: UNIDO

TABLE 7. MAXIMALLY ADMISSIBLE CONCENTRATIONS (MAK VALUES) OF GASEOUS HARMFUL SUBSTANCES IN THE WORKING ENVIRONMENT AT A DAILY EXPOSURE OF 8 HOURS

Chemical substance	Concentration mg/m^3
Acetone	2,400
Formic acid	9
Ethyl acetate	1,400
Butyl acetate	950
Butyl glycol	100
Butanol	300
Cyclohexanone	200
Dichlorethane	80 suspected carcinogen
Ethanol	1,900
Ethyl glycol	75
Dioxane	180 suspected carcinogen
Dimethylformamide	60
Dimethylamine	18
Formaldehyde	1.2
Ammonia	35
Isopropanol	980
Methanol	260
Methylenechloride	360
Perchloroethylene	345
Trichloroethylene .	270
Hydrogen Sulphide	15
Sulphur Dioxide	13
Formic Acid	9
Toluene	750 suspected carcinogen
Ethyl Acetate	1400
Dust	8 suspected carcinogen

TABLE 8. COMPARISON OF DISCHARGE STANDARDS FOR TANNERY WASTEWATERS FOR SEVERAL COUNTRIES

Parameter (mg/l unless other)	**Brazil**	**Denmark**	**France**	**Germany**	**Hungary**	**India**	**Italy**	**Netherlands**	**Switzerland**	**UK**	**USA**	**Japan**
pH units	5.0-9.0	6.5-8.5	5.5-8.5	6.5-9.5	5.0-10.0	5.5-9.0	5.5-9.5	6.5-8.5	5.5-8.5	6.0-9.0	6.0-9.0	5.0-4.0
Temperature °C	40	30	30	35			30	25	30	25		
BOD_5	120		40-200	20-25		30	40	50	20	20-130	40	160
COD	360			200-250		250	160					160
Susp. solids	130	30	30-100		50-150	100	80	80	20	30-80	60	200
Sulphide	1.0	2.0	2.0	1.0	0.01-5	2.0	1.0		0.1			
Chrome (III)		1.0	1.0	1.0	2.0-5.0	2.0	2.0		2.0	2.0-5.0		
Chrome (VI)		0.1	0.1	0.5	0.5-1.0		0.2		0.1	0.1		
Chrome total	0.5							0.05			1.0	2
Chloride							1200	1200	200		4000	
Sulphate		300				1000	1000	150				
Ammonia	1.5	2.0	15-80	5-10	2.0-3.0		15			100		
Phosphorus	1.0						10					10
TKN		5.0	10-60					3.0				
Oil/grease	30	5			8-50		20		20			30

SOURCE: UNIDO/UNEP

TABLE 9. SUGGESTED MAXIMA FOR TRIVALENT CHROMIUM IN SOILS AND SLUDGES

Parameter	Raw Waste (mg/l)	Secondary Effluent (mg/l)	Percent Removal
BOD_5	1100	20	98
COD	3390	249	93
Cr	19.5	0.27	99
Total N	408	270	34
NH_3-N	264	248	5

SOURCE: UNIDO/UNEP

TABLE 10. COMPARISON OF DISCHARGE STANDARDS FOR SEWER SYSTEMS FOR SEVERAL COUNTRIES

Parameter (mg/l unless other)	Brazil	Denmark	France	Germany	Hungary	Netherlands	NewZealand	Switzerland	UK	USA
pH units	5.0-9.0	6.5-9.0	6.5-9.0	6.5-10.0	6.5-10.0	6.5-10.0	6.0-9.0	6.0-9.5	6.0-10.0	6.0-10.0
Temperature °C	40	35	30	35		30	55	40	40	
BOD_5			1000			no limits				
COD									3000-6000	
Susp. solids			500		75				500-1000	
Sulphide	5.0			2.0	1.0		1.0-5.0	1.0	5.0	24
Chrome (III)	5.0				5.0			2.0	5-10	8-19
Chrome (VI)				0.5	1.0	0.0			0.5-1	
Chrome total		2.0		3.0		2.0	5.0-50			
Chloride				600						
Sulphate					400	300		300	1000-1200	
Ammonia					200					
TKN										
Oil/grease	100			250	60				50-500	10

SOURCE: UNIDO/UNEP

TABLE 11. COMPARISON OF SLUDGE RE-USE STANDARDS FOR SEVERAL COUNTRIES

Parameter	Denmark	France	Germany	Holland	Belgium	Norway	Sweden	Switzerland	USA	Engl. & Wales
Maximum permissible soil concentration (mg/kg)	100	150	100	100*	150					600
Maximum permissible sludge concentration (mg/kg DS)	100	2000	1200	500	500	200	150	1000	1000	
Suggested annual loading limit for Cr (kg/ha/yr)		6.0	2.0	1.0	2.0	0.4	1.0	2.5	20-120	
Maximum recommended metal loading (kg/ha)		360	210	100		4			100-600	1000
Maximum sludge solids loading (t/ha)			167	200		20	5 in 5 yrs			
Suggested maximum annual sludge solids application (t/ha)	1.5	3.0	1.7	2 (arable) 1 (grass)		2	1	2.5		
Minimal application period (yrs)	20		100	100		10	5			30
Minimal soil pH		6.0							6.0	6.5**

* Varies according to clay content, eg 50 + (2 x % clay) = max. permissible soil Cr concentration

** The pH quoted is for arable land - for grassland, minimal pH is 6.0

SOURCE: UNIDO/UNEP

TABLE 12. CAPITAL AND OPERATION COSTS FOR TREATMENT AT SOME US TANNERIES

Tannery	Flow (m³/day)	Total Capital Cost[2] To Upgrade Facilities To BPT ($)	Credit Allowed for Existing Treatment Facilities[2] ($)	Annual O&M Cost[1] ($)
1	360	944 000	0	138 100
2	114	150 000	378 400	57 700
3	246	93 000	592 600	73 000
4	3200	2 016 000	971 000	692 000
5	3860	1 327 000	1 118 600	570 800
6	242	290 000	495 000	108 800
7	549	547 000	670 000	189 300
8	1400	344 000	1 446 000	221 600
9	1260	1 161 000	1 319 700	521 900
10	871	12 000	1 843 300	303 300
11	182	543 000	483 100	198 200
12	189	0	665 200	65 800
13	18	0	273 700	34 100
14	1590	1 541 000	165 400	274 300
15	1550	24 000	2 132 500	423 200
16	541	300 000	1 304 200	332 000
17	712	1 303 000	0	174 300
Total	16 900	10 595 000	13 858 700	4 378 400

[1]*Based on tannery operating at 100% capacity.*
[2]*Adjusted to reflect local conditions.*

SOURCE: US EPA, 1982

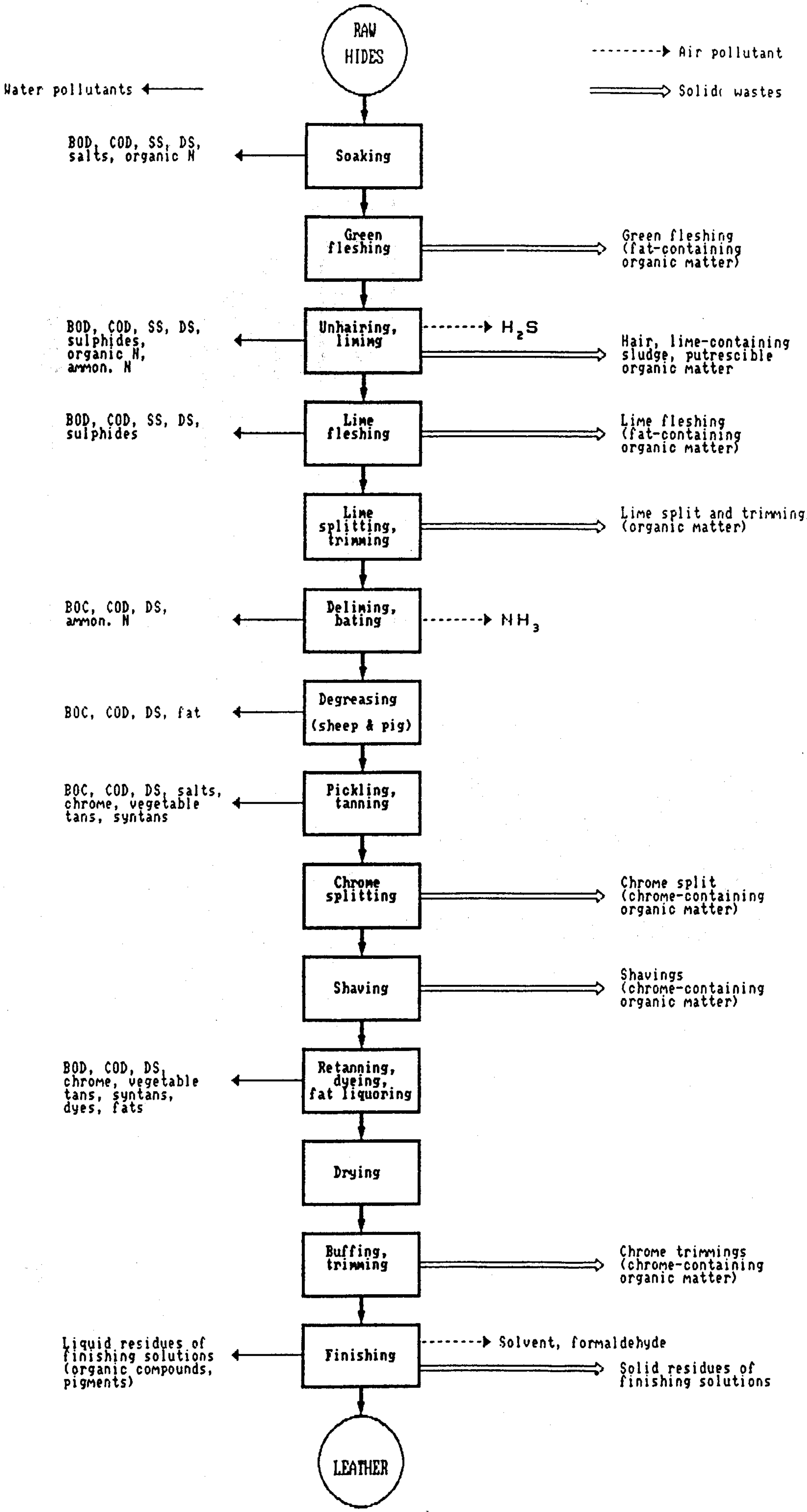


Figure I. Schematic tanning process

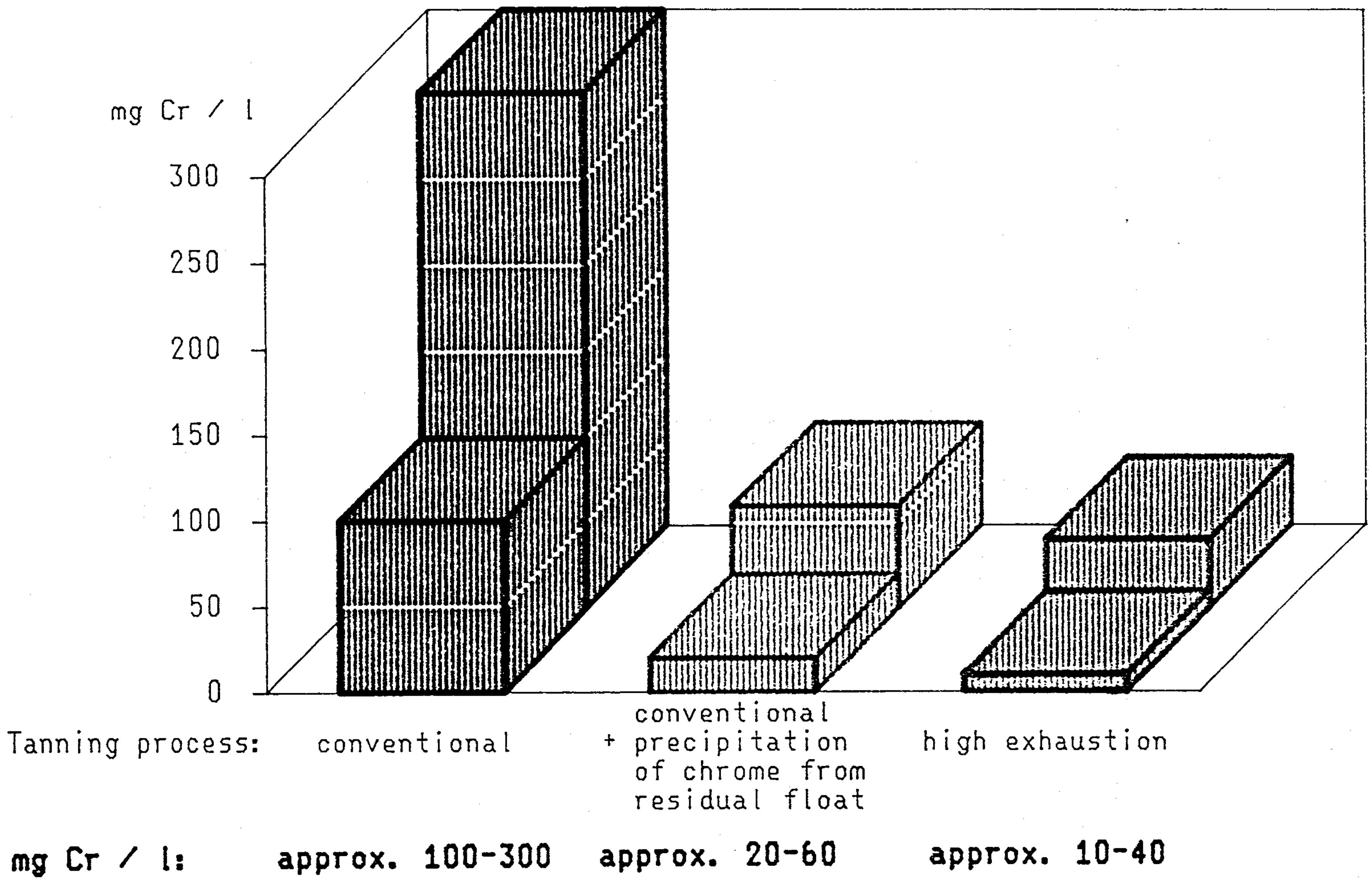


Figure II. Chrome emissions in tannery effluents
Source: B. Wehling et al. (Bayer), 'Alternatives to Chrome Tanning - the Current Situation, 20th Congress of the International Union of Leather Technologists and Chemists (IULTCS), Philadelphia, 1989.

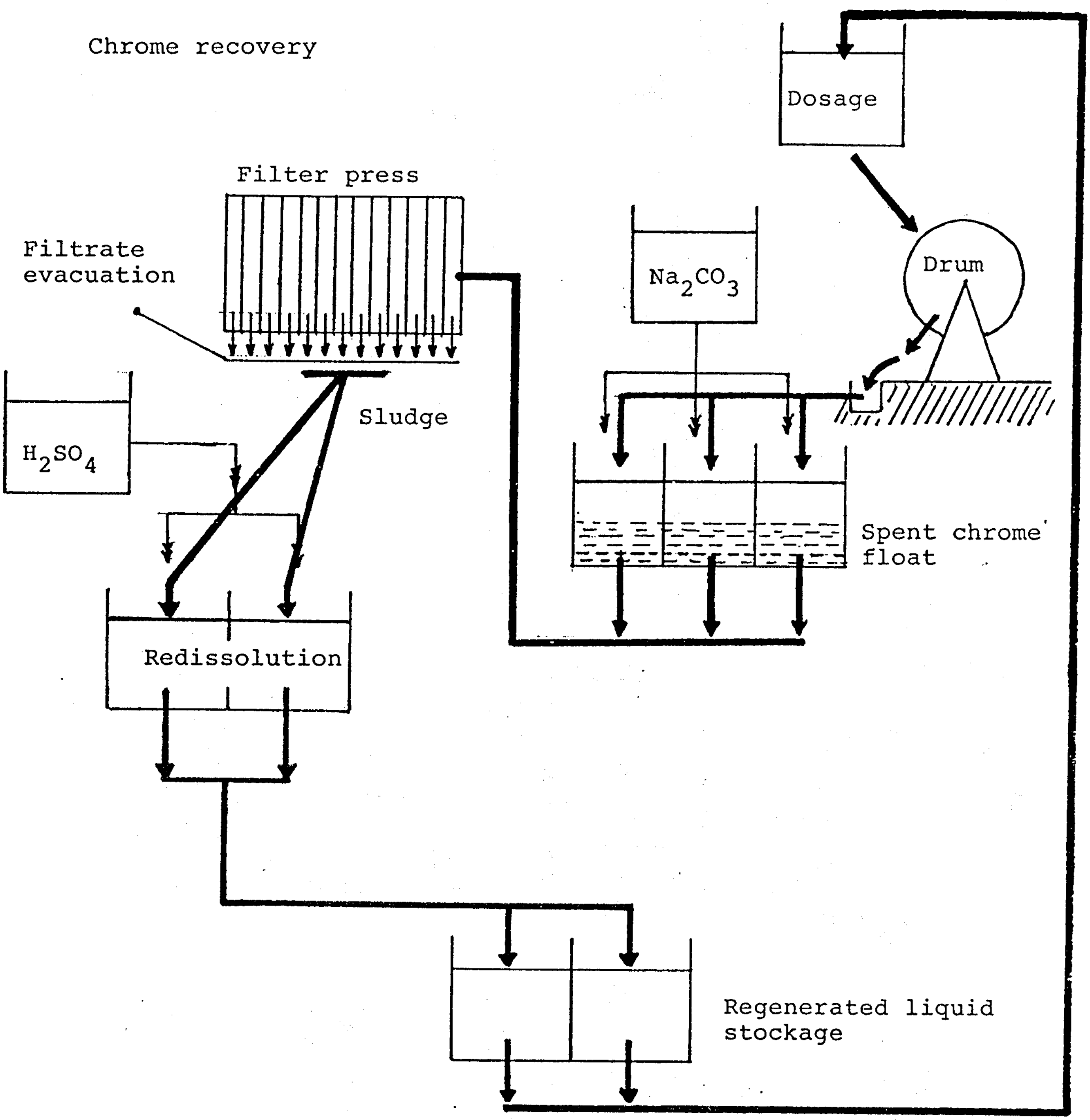


Figure III. Chrome recovery
Source: UNIDO

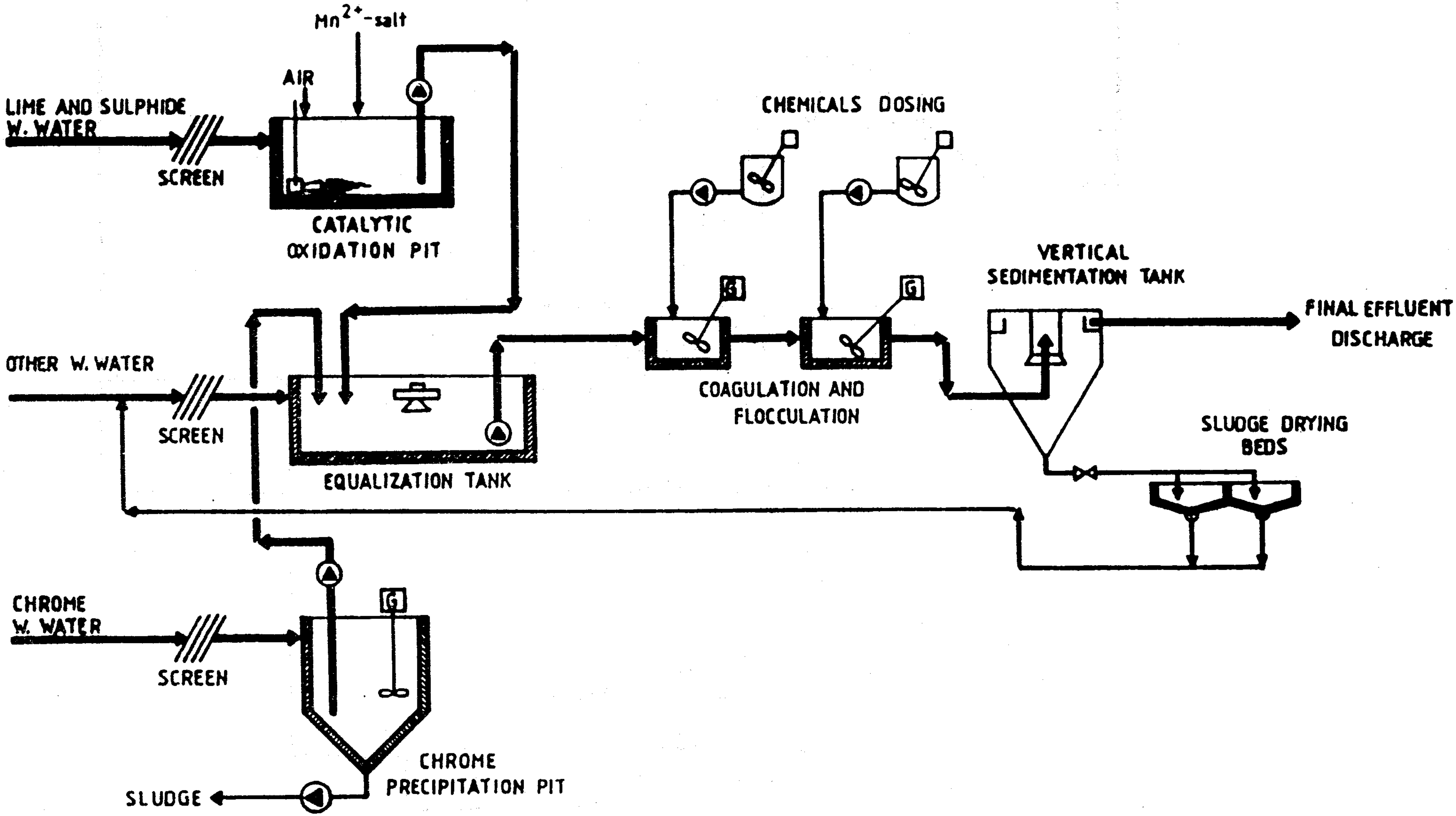


Figure IV. Typical scheme for physical-chemical treatment
Source: UNIDO/UNEP

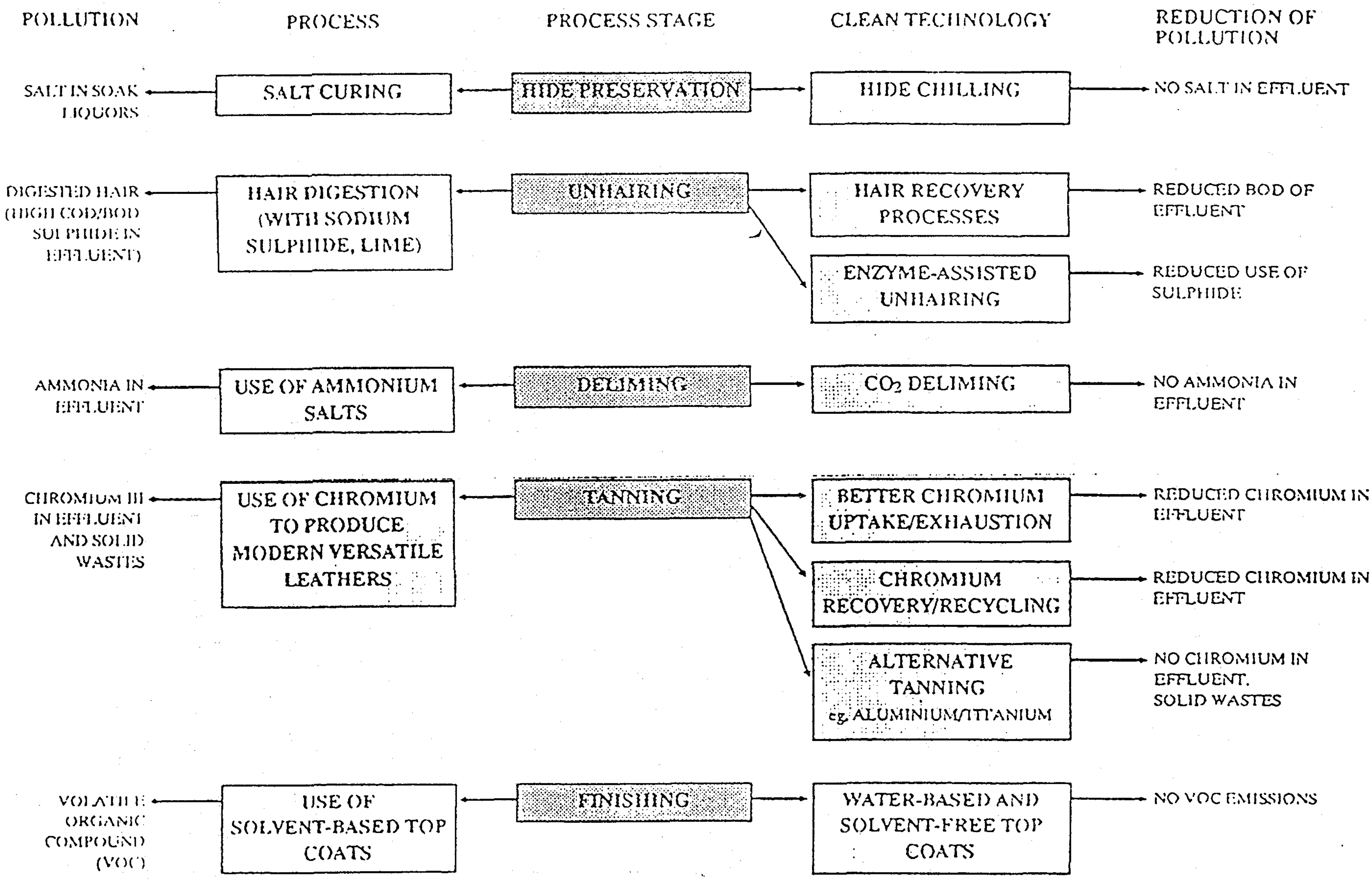


Figure V. Some proposed clean technologies for leather productions
Source: R.L. Sykes et al. 'Environmental Safety Issues - Clean Technology and Environmental Auditing', IX Budapest International Congress on the Leather Industry, October, 1990.

BIBLIOGRAPHY

International Meat Market Review, June 1990, published by the Meat and Livestock Commission, P.O. Box 44, Winterhill House, Snowden Drive, Milton Keynes, MK6 1AX, U.K.

Landell Mills Commodities Studies, 'Leather to the Year 2000'.United States Department of Agriculture, Commodity and Marketing Programmes, Foreign Agricultural Service, Dairy, Livestock and Poultry Division publication 'World Livestock Situation', Washington, D.C., U.S.A.

R.L. Sykes et al, Environment Safety Issues - Clean Technology and Environmental Auditing, IX Budapest International Congress on the Leather Industry, October, 1990.

Technische Anleitung zur Reinhaltung der Luft - T. A. Luft, Federal Ministry of Environment, Bonn, Germany, 1986.

Guidance for Animal and Plant Treatment Processes, UK HMIP, First Draft (3), July, 1990.

Control Strategy for Emission of Volatile Hydrocarbons, Ministry of Housing, Physical Planning and Environment, The Hague, 1989.

United Kingdom Department of the Environment, Circular 7/89, 30 March, 1989.

Pentachlorophenol Pollution Decree, Federal Law Gazette, 12 December, 1989, BGB.1, 1989, 2235, Germany.

Ullman's Encyclopaedia of Industrial Chemistry, Vol. A7, S.93, Verlag, Chemie, Weinheim, Germany, 1986.

Das Leder, G. Schmidt and W. Pauckner, 35, 1984, p.165.

Feliderm CS(R) Process, Hoechst AG, Leather Department, applied in conjunction with Bayer's Baychrom C(R) Process - a high exhaust chrome tanning system.

Radiation Curing of Leather Finishes, Scholnick, Joint American Leather Chemists Association, 1990, 85(2), p.42.

A Method to Convert Tannery Sludge into a Soil Extruder, R. Langlais & S. Shivas, Joint American Leather Chemists Association, 1989, 84(1), p.14.

Leaching Characteristics of Tannery Wastes with Respect to Landfill Co-disposal, I.G. Mason, D.M. Budhia and R.M. Larkin, Joint Society of Leather Technologists and Chemists, 1990, Vol. 74, p.46.

Water Reclamation from Tannery Effluent, A. Bilyk & R. Szpadt, Joint Society of Leather Technologists and Chemists 1990, Vol. 74, p.41.

New Uses of Untanned Hide Collagen, a Mini-Symposium, Joint American Leather Chemists Association, 1980, 75 (11).

Further Non-Leather Uses of Tanned and Untanned Collagen, Joint American Leather Chemists Association, 1982, 77(6).

Simultaneous Pollution-Free Conversion of Machine Fleshings into Protein Meal and Tallow, H. Andres, K.H. Munz and F. Elsinger, Das Leder, 39, (1988), p.101.

Fat and Protein Recovery from Solid Tannery Wastes, A. Simoncini et al, Cuoio 1989, 65(1), p.24.

Animal Feedstuff from Chrome Shavings, M. Alves Dos Reis & V. Beleza, Joint Society of Leather Technologists and Chemists, Vol. 75, Jan-Feb. 1991, p.15.

Pocket Book for the Leather Technologist, p. 318, published by BASF Aktiengesellschaft, Ludwigshafen, Germany.

Report of Meeting of the IULTCS Environment and Waste Commission, May 1987, Joint Society of Leather Technologists and Chemists, Vol. 72(2), p.72.

Guidelines for Upgrading Effluent Quality from Taiwanese Tanneries, David Hayward, World Leather, April/May 1990, p.24.