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Third Consultation on the Leather and Leather Products Industry Innsbruck, Austria, 16-20 April 1984

TECHNO-ECONOMIC STUDY

ON MEASURES TO MITIGATE THE ENVIRONMENTAL IMPACT OF THE LEATHER INDUSTRY, PARTICULARLY IN DEVELOPING COUNTRIES*

prepared by

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1174

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^{} Hove, Sussex, England.**

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The body of this paper was prepared in 1982. However, the "Equipment Available" and their prices as given in Annex IV were compiled in January 1984. Note:

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CHAPT	ER I	
SUMMARY	AND	INTRODUCTION

A SUMMARY

The Study based on a literature survey and field visits, briefly reviews traditional tannery technology and outlines the possible environmental effects of the solid and liquid discharges from typical tannery operation. The conclusion is drawn that two specific constituents of tannery effluent, sulphide and chrome, together with a high organic load characterise tannery effluent and earn the poor environmental image held by the industries' discharge.

The introduction of improved processing technologies is proposed to lessen the environmental impact of effluent discharges and minimise the need for final effluent treatment. Possible methods to reduce water consumption are outlined but it is concluded that the economic benefit of such techniques may be doubtful, unless combined with other measures. Details are given of several recycling processes proven in practice, which would greatly reduce levels of sulphide and chromium in tannery vastes and yield significant economic advantage due to savings of chemical offers.

For circumstances where the reduction in pollutant, due to implementation of improved technology would still not yield an acceptable discharge level, outline details are given of relatively simple, standard, low cost, phsico-chemical means to treat tannery effluent so as to remove up to 95% of the suspended solids and 70% of the organic load, as represented by its Biochemical Oxygen Demand $(B.O.D_5)$. It is considered that in most circumstances prevailing in Developing Countries such treatment should yield a satisfactory standard for tannery effluent discharge to surface waterways.

Although the study expresses some reserve regarding the installation and operation of secondary biological treatment systems in Developing Countries, except where high supervisory and operational expertise is available, a secondary treatment installation employing an "oxidation ditch" is reviewed, and it is concluded that such plant may be the most robust biological treatment system currently available and could be

- ! -

employed in Developing Countries to further lessen the pollutant concentration of effluents where the physico-chemical method outlined earlier does not reach the levels of purification required by local circumstances.

B INTRODUCTION

The tanning and associated industries have from time immemorial been reputed to be major sources of environmental nuisance, both water and air-borne. In recognition of this inudstrial stigma, and following the United Nations commitment in this field, highlighted at the Stockholm Conference on the Human Environment of 1972, the United Nations Industrial Development Organisation in association with United Nations Environmental Programme in 1974 prepared a Study: "Environmental Considerations in the Leather Producing Industry". ⁽¹⁾ * Such Study was of a "background and stocktaking" nature, attempting to review all aspects of the situation, together with outlines of possible mitigating actions.

With the passage of time, since the above Study, the tanning industry has in many areas of the world, devoted much endeavour to mitigating its negative environmental impact, research work has expanded in this field with the results often being proven at operational tannery level.

The growing ewareness of environmental aspects of industry has led to increasing concern by Governmental authorities, in many Developing Countries, regarding environmental pollution by industry, and has focussed on means and degree by which such pollution may be lessened and its economic impact assessed. In many Developing Countries stringent tannery effluent controls have been introduced or proposed, often simulating discharge standards effected in Developed Countries. This has led to consternation amongst tanners who are unable to obtain guidance as to which of the multitudinous systems, outlined in research papers or promoted by commercial interests, should prove most efficacious.

Thus, in order to overcome this situation and to update and reorientate the earlier Study, the consultant was asked to prepare a comprehensive Study "....which should outline strategies and technologies to reduce environmental degradation, conserve water resources and yet

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^{*} For reference please see page 152.

minimize the burden to the leather producing industry to allow controlled development in this particular industrial sector which is of considerable importance to a number of Developing Countrics having suitable raw material resources for such industry".

C OBJECTIVES

The major immediate objectives are to :

- summarize available knowledge in this specific field and update the specialized technology to encompass a variety of new process and tannery effluent treatment techniques;
- outline, in more detail possible effluent treatment and processing technologies suitable to Developing Countries and the relevant techno-economic implications;
- assist governmental planning in this area;
- offer entrepreneurs and developers in Developing Countries guidance with respect to all aspects, technical as well as financial, of improving the environmental impact at new and existing tanneries.

The Study does not attempt to offer any new processes or theories, rather, based on literature, surveys and personal experience, it is an attempt to analyse and simplify the current situation. The Paper is primarily directed towards those Developing Countries who have only limited expertise in this field. It is hoped that the material presented, will assist selection of appropriate technologies.

It is felt that in most situations, be it at tannery, or district or national level, "environmental mitigation teams" should be formed, consisting of tannery technologists, tannery chemists, civil and chemical engineers, together with representatives of local authorities. Such teams should analyse the technology currently employed and all relevant factors utilizing this background paper, and if necessary, the referenced Papers quoted should be obtained to deepen the available knowledge. A major objective of this Paper is to summarize the possibilities available, in a form acceptable to the working tannery technologist, who does not have access to the relevant journals in this field.

As this Paper is directed towards a wide variety of personnel:-Water and Health Authorities, planning officials, entrepreneurs, together with engineers, tannery technicians and others it is necessary in some areas to treat the topic on several levels.

D. LIMITATIONS

Some major constraints in this Study must be noted :-

1. Given the wide area of the subject and the limitations of volume of this Paper it is self-evident that only a limited number of possibilities may be outlined. In general, the consultant, who has in recent years viewed upwards of 100 tannery effluent plants, has attempted to detail only such systems as have been seen working in conditions applicable to Developing Countries, or such other systems as have received universal acknowledgement regarding operational reliability. However, in order to aid those who wish to investigate or install other systems, references are given, enabling further data to be easily obtained.

2. In some areas of both tanning and effluent treatment technology, divergent views are held by authorities in this field. The consultant would suggest that such lack of uniform experience may be due to non-uniformity of tannery technology and effluents, nonstandard equipment and facilities as well as variation in ambient conditions. Given such circumstances the consultant will not attempt to pontify.

3. Given the wide divergence in types of leathers produced in tanneries, technologies employed and the environment into which effluent will ultimately be discharged, it may be accepted that in general the consultant refers to a typical average tannery, producing an effluent similar to that outlined at Annexes IA and B. Traditional water usage in tanneries has in the past greatly exceeded 50 litres per kilogram Wet Salted Hide (litres/kg). Modern technology could yield usage of (15 litres/kg. However for discussion purposes a
nominal process consumption of 30 litres/kg is assumed, as a realistic
average, which could yield total water usage of 45 litres/kg.

4. In general, the consultant, accepting the impossibility of proposing definitive technology and specifications, feels that, given an understanding of the rationale of the options, a competent team should be enabled to prepare the specifications for any necessary scheme be it an alteration in process to minimize pollution (install "improved environmental technology"), or the installation of necessary effluent treatment plant.

5. This Paper is directed towards Developing Countries, which are often categorized by the limited availability of experienced technical and control personnel, as well as constraints regarding availability of servicing and spares. Mindful of this situation the consultant does not propose and/or detail highly sophisticated, automatically controlled plants. In this connection, it may be noted that the writer has personally closely examined several large, fully automated treatment plants in Africa (each costing) U.S.\$ 2 million to install/ construct) which were non-operational due to lack of competent supervisory personnel (aggravated by poor or non-existent operational manuais). Such complex automated units, although suitable in Developed Countries could not be considered "appropriate technology" It must also be noted that a few Developing where installed. Countries have fully developed leather industries, with an abundance of qualified technical personnel and may, within the leather sector, be considered "Newly Industrialized Countries" (N.I.Cs). (Part of Latin America and Indian sub-continent). This Paper is not directed towards such areas as it is felt that they have sufficient expertise in the field to analyse the experiences of others and draw their own conclusions.

6. This paper outlines technologies suitable for industrial and semi-industrial tanneries, creating some 50 m^3 /effluent day or more, and is not directed towards rural pot or bag tanners whose typical usage may be only some 1 - 5 m^3/d for whom no technology apart from lagooning may be recommended.

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CHAPTER II

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TRADITIONAL TANNERY TECHNOLOGY, TANNERY WASTES, POLLUTION

A TRADITIONAL TANNING TECHNOLOGY

1. INTRODUCTION

It must be appreciated that leather making, even in highly Developed Countries, is today still much of an industrial art with tannery managers and technologists employing their own personal processes. Similarly plant and equipment vary from tannery to tannery, as will capacity of production unit and end-product. Thus, although some basic similarity exists there can be no universal definitive or even "basic" tannery process.

Given these variations in utilized technology it is not uncommon to find variation in particular detail, thus water usage may range from

 $\langle 20$ litres/kg hide to $\rangle 100$ l/kg, consequently the effluents from such process may vary equally widely in concentration of pollutants. Discussion in this Paper must therefore outline guidelines and strategies which need adapting to conform to local circumstances. For those not conversant with tanning technology this chapter contains a brief review of a typical leather technology.

2. GENERAL

In addition to variations due to personal choice of technology wider technological divergence is caused by the need to satisfy the end-product requirement characteristics. Although some major sequences may be parallel, certain speciality leathers may employ individual technologies (e.g. oil tannage for chamois). However, Chrome Tanned Shoe Upper Leathers are still today the major tannery product, and their processing will be the general background process referred to in this Paper. Fig I, overleaf, outlines a typical simplified flow chart of major tannery activities, from which may be seen the large number of processes entailed during the Batch production is still the basic production of a basic leather. system employed. Size of batch is normally governed by the capacity of wet work processing vessels, usually "Drums" (large wooden cylindrical vessels, - size, varying from 1 - 5 m. height and width, with capacities ranging from a few kilos to 20 m.t. or more - rotating at 2 - 12 r.p.m. according to process). Newer installations may have replaced these

wooden vessels by steel and fibreglass units and sometimes inclined processors are employed (similar to large concrete mixers). Paddles (horizontal open topped, semi-cylindrical vessels with wooden rotors) may be employed for calf or skins from petty rumiants. Such alternate process vessels up not however, per se, radically affect the technology employed, howaver, it may be noted that the newer process vessels usually allow lower levels of water utilization (with concomitant increase in concentration of pollutants), whereas "paddles" employ high levels of water utilization (with reverse effect on concentration of pollutants). (See Chapters III and IV).

Annex II shows a "Typical Outline Process" with chemical inputs which from a tanner's viewpoint may have been considered "modern", circa 1970, but which may be considered "unsound environmentally" today.

FIGURE I SIMPLIFIED OUTLINE FLOW CHART OF TYPICAL TANNING TECHNOLOGY											
	\overline{O}	- OPERAT		= 1NS!	PECTION	\Box	= TRANS	FORT	=s	TORE	
Hides	A Hides	3 Hides Match in	L Soak in Pite un	5 Haul	6 Cut	(7) Green Flesh	Transport to	(9) Complete	10 Lime 21 hours	11) Haul	$\begin{array}{c} 12 \\ \hline \end{array}$
Inspect & Grade	Stored	packs, Transport to soak	to 48 hours		Sides	on Machine	Drums	in Drum Dry Drum	Depila- tion in Drum	<u> </u>	
	L. Transpor	15 t. Dalime	16 Bate	(17) Pickle	(18) Tan	(19) Basify	20 Test	21) Pile 24 hr	WET 1	22 Sammy	$ 23 \rightarrow $
by Hand	to Drum	(A series	of sequer carried	ntial chem out in aque	ical ope sous med	prations (Thermal Stability	to allow Hydrolysis and Chrome Firstion	ETION OF EUUE PHASE	by Machine	by Machine 1.6 mm
(24)	25	26	27	28	29	30	(31)	<u>(</u> 2	(33)	(J4)	$\square \rightarrow$
Shave by Machine	Select and Weigh	A series of operations aqueous mod	Retan of sequent: carried o	Fat Liquor ial ut in	Haul	Sammy/ Set by Machine	Vacuum Dry by Machine	Pole dry by Machine	Stake by Machine	Measure by Machine	Store After Grading = <u>CRUST</u> <u>LEATHER</u>
36	37	38) NIST	39 IMERICANA T			L2 SPRAT	L3 PLATE	SPRAT	LIS MEA STIPPE	LL6	
by Hydraulic Press	by Machine	by Machine	by Spray	by Hydraulic Press	by Hand	Tvice	or Enboss	Topcost	NEA SURE	UTAUE	FINISHED LEATHER

3. MAJOR PROCESS SEQUENCES

The choice of chemicals to be utilized is exhaustive, below each sub-section may be found a note of some possible agents employed (individually or in admixture). Percentage offers relate to weight of hide or skin with the exception of solutions.

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a) Curing of Hides and Skins

In most Developed Countries hides and skins are removed and lightly cured with salt at abattoirs or local hide collection centres - throughput is relatively regular and technical supervision is available, the hides and skins then enter commercial channels and are transported, generally relatively short distances, to tanneries for processing.

In many Developing Countries however most animal slaughter takes place at rural village site. The production of hides and skins is usually at a low and erratic volume, governed by seasonal conditions and accordingly in these circumstances, only minimal supervision may be available at the curing site. With high ambient temperatures often encountered curing is not simple. Salt, if available, is applied and the skins then dried (Dry Salting), only in a few Latin American Developing Countries is salt curing carried out efficiently, i.a. "wet salting" whereby the hide is immersed and saturated with brine solution. Unfortunately many Developing Countries are deficient in cheap salt supplies and consequently curing is by drying (varying condition and degrees of drying). Unless such drying is well controlled, degradation of the hides and skins may occur. The major drawback of "drying" is that the tanner must subsequently attempt to reverse the process (rehydrate) during soaking (employing large volumes of water). Curing often incorporates treatment with insecticides, in minute quantity to discourage beetle and other insect attack during storage and transport,

(Possibly: - Pyrethem, p-dichlor-benzene, D.D.T., benzene hexachloride, sodium silico-fluoride, solutions of arsenious oxide (0.15%), emulsified dieldrin 0.075% et al.)

b) Soaking

Soaking which may be carried out in pit, paddle or drum (or combination), is to rehydrate the skin and reverse the cure process. Duration up to 48 hours, dependent on degree and type of cure and ambient temperature. Dirt, blood and dung may also be removed.

 $(0.2 - 2.0 \text{ gas per litre of float sodium hydroxide, sulphide or sulphite$

Up to 1 gm/l sodium hypochlorite and/or 0.5 - 2.0 gms/l wetting agents, emulsifiers, surfactants and/or ensyme preparations.)

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c) Liming

This process traditionally utilized large quantities of Lime blended with sodium sulphide to loosen wool and hair, or dissolve these into a pulp, additionally the process opens the fibre structure and "plumps" the hide. The duration of the process may vary from 18 hours (drum) - 7 days (pits).

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With skins whose hair or wool is potentially of high value the depilation may be effected by "painting" the flesh side of the hide or skin with a mix of lime or kaolin plus sodium sulphide. After piling for some hours the hair roots may be attacked and the wool may be removed without being seriously contaminated by the chemicals. Such "hair save" process however needs a subsequent liming (alkaline treatment, possibly sulphide free), to accomplish the necessary adjustments to fibre structure.

Hides and skins may be split in the limed condition, yielding a "grain" leather of level substance, such lime splitting allows more economic and rapid later processing, however, due to the technical difficulty of this process it is often carried out in the tanned condition.

(2 - 10% calcium hydroxide (Lime)
+1 - 4 \$ sodium sulphide, sodium sulphydrate
Possibly small amounts of ammonia, caustic soda, di-methylamine sulphate.

Recently enzymatic preparations have also found limited employment.)

d) Fleshing

The physical removal of adipose tissues from the flesh side of the hide. (The resultant fleshings are difficult to handle due to their mucuous-like condition, and the unavoidable presence of large volumes of water from the machine).

e) Delime

The removal of lime from the hide (not always completed through the full thickness of the hide).

Copious washing (in drum or paddle stc) is followed by

neutralizing chemicals. Traditionally, the washes were with liberal volumes, utilizing an open water valve for a set period (somewhat inefficient as water discharge not constant or measured). (See Chapter III).

(Acids, 0.5 - 2.0%, sulphuric, hydrochloric, lactic formic, boric (possibly mixtures), acidic salts, ammonium chloride or sulphate, sodium bisulphite.)

f) Bating

An enzymatic process which has pronounced effect on the grain of the hide or skin and general run and stretch of subsequent leathers. Possibly accomplished by acting on the elastin network of the grain, the degraded protein (partially attacked during liming) and the erector pili muscle. The current enzymatic aqueous treatment employing 0.5% bating material, of $\frac{1}{2}$ - 12 hours duration in drum or paddle replaces the age-old processing which entailed treatment with dog dung or pigeon droppings.

(The "bating material" itself is usually composed of :-

- 50% Wood flour or other carrier

- 30% Deliming Agent (ammonium chloride) 1 - 5% Pancreatic Enzyme)

g) Pickling

An adjustment of the pH of the pelt, sterilizing the skin, ending the bating action, allowing penetration prior to subsequent fixation of the tanning material.

(5 - 10% common salt (sodium chloride) or sodium sulphate 0.6 -1.5% acid (sulphuric, hydrochloric, acetic or formic or mixtures). Possibly 0.01% fungicide:- para-nitro-phenol or B-napthol).

h) Tanning (See Glossary - Annex III)

The tanning process converts the collagen, the major constituent of the hide, into a non-putrescible condition, in addition, tanning imparts the necessary "feel" and chemical and physical characteristics to the leather.

(1) Chrome the majority of leathers are today chrome tanned in drums for $\mu = 2\mu$ hours employing :-

(8 - 12% Chrome tanning salt (Basic Tri-valent Chromium Sulphate hydrated complexes) (22 - 25% Cr_2O_3)

1.0% sodium bicarbonate (basifying agent to adjust pH) 0.1 - 0.5% masking agent - Sodium formate, Phthalate or salts of Dicarboxylic acids

0.1% fungicide if product is to be stored/transported in wet blue condition).

(ii) <u>Vegetable Tannage</u> Has been eclipsed by chromium as the major tanning material. However, is still employed for sole and saddlery and some speciality leathers.

1 day (drum) - 6 weeks (in pit)

(Employing 15 - 30% of commercial tanning extract (Bark or wood of tree, aqueously extracted then spray dried or concentrated).)

(iii) <u>Syntans</u> Are increasingly employed as auxiliaries in association with chrome and vegetable tannins, or may be employed as principal tanning agents for certain speciality leathers.

(1 - 25% of syntam may be employed, according to function, such materials are typically sulphonated condensed products of phenol, cresol and naphthalene or resins).

(iv) A wide variety of alternate tanning materials are available for use as primary tanning materials, or as auxiliaries with chrome, vegetable or others, but as yet the volume employed is limited and seldom have been reported as having significant effect on tannery effluents; and these include :

(Zirconium salts, formaldehyde (chamois), Cod Oil (chamois), Glutaraldehyde)

i) Post Tanning Activity

Following tannage certain physical operations are completed, these in general aim at levelling the substance of the irregular natural material.

(i) <u>Sammy</u> by machine (pressurized rollers) to remove excess moisture.

(ii) <u>Split</u> by machine, if not carried out in lime condition. or

(iii) <u>Shaving</u> whereby substance is levelled, the surplus material yielding a waste of small fragments, (rather than the sheet-like material obtained from splitting).

The above physical processes are in preparation for subsequent :-

(iv) <u>Neutralize</u>, <u>Retan</u>, <u>Dye</u>, <u>Fat Liquor</u>. During these processes, often sequential, in a drum, employing a common bath, the final colour, feel and characteristics of the leather are obtained. Employing :-

Neutralizing	1% Mild Alkeli or Syntan			
Retan	A wide range of tanning materials,			
	previously noted.			
Dye_	1 - 6% acid, direct, basic or			
	speciality dyes.			
Fat Liquor	3 - 10% sulphated or sulphonated fish,			
	vegetable or animal oils, as well as			
	mineral and "synthetic oils".			

j) Drying and Finishing

The leathers are sammyed to remove moisture. Set out to eradicate creases and folds, then dried. The final finishing process, (as may be seen in Fig. I) includes mechanical treatment of grain and flesh followed by application of surface finish. These processes do not generate significant effluent, and may be of minor interest in this Paper.

4. WATER UTILIZATION

a) Interoperational Weights

From the "typical" process shown at Annex II it is not easily discerned what volume of water is utilized. This is due to the leather industries age-old system of calculating process volumes (floats) as a percentage of the weight of the goods. Normally such floats are calculated on weighings at two strategic process points, i.e. limed and fleshed = <u>Lime Pelt</u> weight

Tanned, split and shaved * Shaved weight

This basis of calculation, overcomes the problem of the irregular size, shape and cure conditions of this natural heterogenous raw material. However, differing cure conditions

affect the weight basis of processes prior to the Limed Pelt weighing.

Thus:100 kg of Air Dried African Hide could yield250/290 kg lime pelt100 kg of Dry Salted " " " 170/180 kg lime pelt100 kg Wet Salted Hide could yield120/125 kg lime pelt100 kg Fresh (Salt Sprinkle) Hide could yield95/105 kg lime pelt

Much published work concerning water consumption relates to European/N. American, lightly salted hides, and to compare with a tropical air dried material a factor of circa 2.3 must be utilized.

b) Water Utilization

(i) Calculation of process water utilization proves difficult as some traditional processes refer to "running water washes" - this usually inefficiently controlled process, usually timed for 15/20 minutes, may use from 200 - 500% water, but is dependent on the flow rate of the water (often variable), and the time actually employed (not usually accurately monitored). The efficiency (or otherwise) of this system is discussed in the next chapter.

The typical process outlined at Annex II would nominally consume some 26 litres water per kg. lime pelt weight = approximately 30 litres/kg wet salted hide.

However, tanneries have historically been somewhat lavish with water utilization - due to poor control of volumes in works, coupled with large volumes expended on housekeeping (floor and drum washings) thus nominal process usuage of water in most tanneries is exceeded by at least 50%. A nominal consumption of 30 litres/kg could represent an actual usage of \geq 45 litres/kg.

B TANNERY WASTES AND POLLUTANTS

1. SOURCES OF WASTES AND POLLUTANTS

The tanning industry has for long been stignatised as a "Norious Industry" due to the high quantities of wastes produced, both solid and waterbourne, which are both sometimes characterised by norious odours. However, it must be recognised that, given the carnivorous nature of the majority of society, and the lack of any alternate industry to dispose of, or consume, the hides and skins necessarily yielded as a byproduct of meat consumption, the tanning industry performs a socially desirable function by providing an economic outlet for these materials. Such hides and skins, if not processed by a leather industry, would constitute a far greater environmental hazard than that generated when the hides and skins are tanned, albeit that the hides and skins could putrify at dispersed slaughter locations, while the tanning industry's discharge is more centralized and concentrated.

There are two major sources of waste from tanneries :-

a) Those constituents of the raw hide or skin which are necessarily removed or modified during the tanning process. Including the hair or wool (whole, or pulped or completely broken down and dissolved), various collagenous and non-collagenous proteins removed, natural fats, trimmings, splits, shavings, buffing dust and chemicals which may have been employed during the curing process.

b) Surplus and residual chemicals from the tanning process.

The items under a) above are, given current technology, necessary wastes from the tanning industry, whether or not they can be economically utilized or disposed with minimal environmental nuisance is the major question today.

The residual chemicals of category b) above are to some extent within the control of the tanning technologist. Chapter III ("Improved Environmental Technology"), will discuss the minimisation/eradication of environmental nuisance from this source.

2. NATURE OF WASTES

It is usual to bifurcate tannery wastes into two categories :-

- a) Solid Wastes
- b) Waterbourne Effluent

Howewer, this is possibly an oversimplification, as individual tannery technology may determine whether a particular waste is separated initially as a solid, or discharged with the effluent where it will be accounted part of total solids (e.g. fleshings, shavings, buffing dust appear in varying volumes in liquid discharge - effluent). For convenience, this Paper will discuss these two items separately. This Paper which is directed towards mitigating environmental nuisance from the industry will not overdetail the constituents of the wastes, solid and liquid, as these are available elsewhere $\binom{i}{i}$. However, to allow realistic discussion of "mitigating techniques" an outline of pertinent constituents and major pollutants is given below.

3. SOLID WASTES

a) Quantity

Volumes of solid wastes produced depend greatly on the raw material being worked and the end-product nature. There is little published data comparing solid waste production from differing raw material, but it may be speculated that the production of leather from, say, African dried hides may yield higher levels of solid wastes, as the substance of such raw material varies greatly from flank to backbone, and a higher % of the split obtained is not utilized.

Two recent surveys of solid waste production are outlined below. Frendrup⁽²⁾ studied solid waste at ten Swedish tanneries and three fur dressing units. A U.K. Department of Environment Paper⁽³⁾ outlines a materials balance for the production of Chrome tanned Bovine Leather.

TABLE I	TABLE I SOLID WASTES PRODUCTION				
	FRENDRUP ⁽²⁾ kg dry substance/t * raw material	U.K. Dept of the ENVIRONMENT ⁽³⁾ Indicative quantities of wastes "as arising" kg/1000 kg Wet Salted Hide			
Trimmings	15	120 kg			
Fleshings	41	70 - 230 kg			
Lime Split Waste	2				
Hair, Wool	20				
Chrome Shavings	35	99			
Chrome Split Waste	19	115			
Vegetable Shavings	2	Buffing Dust 2			
Vegetable Trimmings	0-4	Finished Trimmings 32			
Effluent Sludge	15	250			
	149-4*	688 - 848			
(* Note: To some extent this method of recording does not easily relate to the quantity of waste actually arising, as in normal circumstances many of the materials hold significant quantities of water).					

Although these materials are noted as "wastes" to the leather sector some significant volume may be utilized in the manufacture of glue, or as fertilizer. Until the last decade there was significant economic demand for fleshings, trimmings and untanned splits for use as a basis for fat rendering and in the manufacture of glue and gelatine. However, with the advent of synthetic glues and detergents demand for tannery wastes in most countries has slackened. The bulk of solid wastes being generally disposed of by controlled dumping or burying with occasionally small volumes being incinerated.

b) Characteristics of Solid Wastes

The solid wastes from tannery production vary greatly in character according to technology employed and the levels of "housekeeping" instituted within the tannery. A more detailed analysis may be seen in the earlier UNIDO/UNEP Study⁽¹⁾.

From the ecological viewpoint the most significant solid waste characteristics may be :-

(i) The untanned collagenous wastes and fats e.g. raw and soaked trimmings (often mixed with fleshings) which could give rise to odours,

(ii) The sulphide bearing wastes, e.g. trimmings and fleshings, from the hide in limed condition and beamhouse residues and sludges,

(iii) The chrome bearing wastes, e.g. shavings, buffing dust and sludges from equalized effluents,

From an aesthetic viewpoint the piles of unutilizable chrome splits, which often "adorn" tanneries in Developing Countries may be classified as an eyesore, but seldom exert significant influence on the ecological cycle.

Methods of mitigating the environmental impact of these materials will be discussed in later chapters, but it may be noted that many of the techniques for re-utilization of solid wastes require either a high level of investment, a large volume of product, highly sophisticated techniques, developed and/or integrated associated industries, and thus may not be suitable under conditions prevailing in the Least Developed Countries (L.D.Cs). Thus some note must be given here as to the actual significance of these materials. (i) The untanned wastes, with their high protein contents can certainly, if left lying in damp conditions, give rise to odours due to bacterial attack and decomposition, as well as encouraging beetle and insect infestation. However, provided they are not heavily contaminated with process chemicals they are certainly a most suitable material for agricultural fertilizer and, if rapidly removed from the tannery and dug or ploughed into agricultural lands, will rapidly disintegrate and, due to their dispersion, will occasion virtually zero odour or other negative environmental impact.

(ii) Untanned wasstes bearing sulphide, if accumulated may give rise to malodorcus hydrogen sulphide fumes, however, the concentration in this form is unlikely to be hazardous and providing the material is regularly removed from the tannery site and buried or ploughed in, as above, the environmental degradation will be minimal. Beamhouse residues and sludes can likewise be buried, but as the means to remove the majority of sulphide (see Chapter IV) from such sludge is relatively simple, such sulphide bearing material should be eradicated in future.

(iii) Chromium bearing wastes have raised queries from ecological quarters. However, on analysis the toxicity of tannery solid wastes due to the presence of chromium is questionable. Many of the earlier ecologists' comments regarding chromium toxicity refer to Chrome in the Hexavalent form, whereas the vast majority of tanneries today employ the less toxic Trivalent form of chromium. Sludges from effluent treatment may contain up to 3.5% chromium⁽³⁾, leather fragments (buffing dust, shavings, scrap splits etc) may contain 2-5% Cr_2O_3 .

In those N.I.Cs with significant leather sectors (Argentina, Brasil and India), the economic disposal of chrome tanned solid wastes is often possible as a constituent of "leatherboard", however, as yet, such production is not economically practical in most L.D.Cs, thus this end-use is not available to their tanners.

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The chromium in sludges is in an insoluble form and is "virtually insoluble at pH values found in the environment" (3). The majority of chrome within tanned leather fragments is chemically bound to the skin protein and not easily displaced.

Several aspects of the effect of chromium in tannery wastes are under active investigation by leather chemists and others to resolve the conflicting viewpoints. These include :-

Effect of chromium on plant growth and the effect of chromium in a landfill environment.

The U.K. Government report⁽³⁾ states..... "The Ministry of Agriculture and Fisheries Agricultural Development Advisory Service (ADAS) quotes 500 mg chromium per kg of soil as the maximum concentration of chromium in soils which can be tolerated with no adverse effect on crops and the Report of the Working Party on the Disposal of Sewage Sludge to land advises that it would almost certainly be possible to apply over 30 years or more a total of 1000 kg ha of chromium to the soil in sewage sludge, without harmful effects on crop growth. (This is equivalent to a maximum concentration of chromium in the soil of about 500 mg kg⁻¹.). Elsewhere a limit of 500 mg Cr (111) kg is applied to soils of low pH value (pH less than 5.5) but in alkaline soils a level of 1,000 mg Cr (111) kg⁻¹ has been found not to interfere with crop production."....."Experiments have shown.....that reduction from chromium (VI) to chromium (111) occurs spontaneously and rapidly in the presence of soil organic matter, under both acidic and alkaline conditions.... It is concluded that the risks from adding chromium to the soil in organic wastes such that the maximum soil concentration (500 mg chromium kg of soil) is reached, would appear to be negligible".

A recent U.S.A. Paper⁽¹⁾ on the contrary claimed that when Trivalent Chromium compounds were mixed with soil, a relatively rapid oxidation to the more toxic hexavalent state took place. However, several member os the I.U.L.T.C.S. Tannery Wastes Commission were critical of this work, which did not conform to results they had obtained.⁽⁵⁾

Incineration and pyrolysis of chrome bearing materials, a possible alternative to landfill techniques, has been investigated, and reported $\binom{6}{7}\binom{8}{9}$ with regard to their relative efficiency, and their economic and ecological advantage over landfill as a means of disposing of chrome bearing wastes.

The conditions of processing which minimise risk of conversion of the trivalent chromium to the more toxic hexavalent form These require close control of temperature and are detailed. Corning⁽⁵⁾ "pointing out that if chromium other factors. and lime were present together" (as is likely with sludge from mixed tannery effluent) "there was a real danger of producing calcium chromate, a proven carcinogen". The major advantage of incineration and pyrolysis is the possibility of recovering significant quantity of chromium. The practical economics of such systems, some of which are covered by patents, have yet to be generally proven on commercial scale and, in future, may need evaluating against alternate methods of recovering chrome outlined in Chapter III. However such technologies seem outside the current attainment of most developing countries, due to the need for high throughput to justify capital expenditure and need for careful control.

4. EFFLUENTS

a) Volume

Volumes of water utilized by tanners have been lowered in recent years, due to :-

(i) Increased charges for water supplies,

(ii) Attempts to reduce volume and subsequent charges for effluent treatment,

(iii) Institution of lower, or low float, tanning technology in order to obtain more efficient utilization of process chemicals and more rapid production,

Frendrup⁽²⁾ in his survey of Swedish tanneries found water consumption :-

1962	-		$103 \text{ m}^{3}/\text{t}$	(litres/kg)
1975	-		$47 \text{ m}^3/\text{t}$	(litres/kg)
1977	-	about	<u>L0 m³/t</u>	(litres/kg)

The advantages of lower water consumption are selfevident with regard to financial economies. With regard to effluent/pollution concentration the effect is to proportionally increase the concentration of pollutant pro-rata with the reduction in volume. The effect of such increase in concentration and lowering of volume, with regard to effluent discharges, is dependent on the structure and basis of local discharge regulations. In some cases where concentration limits of pollutant have been established the incentive for tanneries to lessen water consumption is negated (see following chapters).

b) Characteristics of Effluent

(i) Theoretical Minimal Pollutants

As outlined earlier at II.B.1 given current technology of tanning, some minimal quantity of materials will necessarily be present in the aqueous tannery discharge. These, mainly due to the constituents of the hide which have been attacked/or reconstituated during tannage, the UNIDO/UNEP Paper⁽¹⁾ suggests :

TABLE II	
MINIMAL INEVITABLE POLLUTION - CHRON	E TANNED LEATHER
1	POLLITION
	zms/kg W/S Hide
INORGANIC (FIXED) SOLIDS	
Hide Salt	150 g/kg
Salts from hide, raw water and sanitary usage	10 g/kg
Total Inorganic	160 g/kg
ORGANIC SOLIDS	
Hair Protein	h0 g/kg
Hide Protein	25 g/kg
Hide Fat and Carbohydrates	15 g/kg
Dirt and Mamure	5 g/kg
Organic substance from raw water and sanitary us	e 2 g/kg
Machine and Building cleaning	3 g/kg
Total Organic	90 g/kg
Total Solids	250 g/kg

Normal tannery effluents however are found to have at least double this theoretical minimum as appreciable surplus process chemicals are unavoidable with current technology.

(ii) Actual Effluents Found

Annexes IA and B detail typical pollutants found in tanneries employing traditional technologies - variations will occur due to differing technologies employed, and the manner in which the various effluents are mixed together in the internal sewers.

Variations in significant pollutants produced and concentration may be seen in Tables III and IV

TABLE III							
REPORTED F	REPORTED POLLUTANTS - TANNERY EFFLUENTS - Kg/ton Raw Hide						
	Annex IA This Paper. Chrome Leather	U.S.E.P.A. Chrome Leather	FRANCE C.T.C. Chrome Leather	SWEDEN (12) Mixed Tannage	POLAND Mixed Tannage		
BOD ₅	60	95	75 - 90	71	70		
COD(K ₂ Cr ₂ 0 ₇)	175	260	200 - 220	190	233		
Suspended Solids	150	140	140	106	70		
Sulphide	7	8.5	9	-	6*		
Chrome	4.5	4.3	6	2.7	1.1		
Volume of Water m ³ /ton	45	53	65	circa 40	70		
*Recorded as H ₂ S							

Note:

<u>Measurement of Pollutants</u> - This may be recorded in two methods :-

 (i) Absolute Terms - i.e. pollutant expressed in relation to weight of original raw hide (usually wet salted condition), i.e. kg (pollutant) per ton (raw material) or gms per kg., (both expressions being equal i.e. parts per thousand).

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<u>TABLE IV</u> CONCENTRATION OF POLLUTANTS - TANNERY EFFLUENT - mg/litre						
Innex I B This Paper Chrome LeatherGorecki (2) Mixed TannagesPoland 						
BOD5	1,300	1,000	1,750			
COD	3,500	3,300	3,400			
Suspended Solids	3,30C	1,000	2,800			
Sulphide	160	85*				
Chrome	100	15	125			
Volume of Water Employed in tannage litres/kg 45 70						
* Reported as H ₂ S						

Note: (Continued)

(ii) <u>Concentration Terms</u> however express the pollutant concentration of the effluent liquor i.e. milligrams (pollutant) per litre (mg/l) or occasionally as "parts per million" (p.p.m.) (again the two terms for practical purposes are synonymous). Measurements by (i) or (ii) above are interrelated by the volumes of water utilized.

(iii) Significance of Effluent Constituents

Currently, in Developing Countries, municipal effluent treatment plants are few and far between, and virtually all industrial effluents, including tannery discharges flow to surface waters. Thus discussion here will mainly concern such discharges. In those Developing Countries where municipal or other public owned treatment works (P.O.T.W.) exist, some measure of expertise in effluent treatment matters exists, and the need for this Paper is diminished. Such detail as is given in relation to surface waters may be adapted by P.O.T.W. engineers. The significance of any effluent discharge and its effect on all environmental aspects will depend greatly on the flow of the recipient, and consequently its ability to dilute and absorb such load with minimal ecological disturbance.

From a practical viewpoint it may be asked, what are the significant pollutants? what is their effect on the environment?

A simplification of the situation would suggest that two specific constituents, chrome and sulphide have some level of potential toxicity in addition to which the general "biological load" may have significant localised effect on the dissolved oxygen content of the recipient waters.

:- Chrome:

Chromium in the hexavalent form is reported to have some effect on aquatic life. Although fish are relatively tolerant towards chrome, fish food organisms and other lower forms of aquatic life are more sensitive. However, tannery discharges of chromium to surface waters do not appear to have been fully evaluated. Such tannery discharges of chromium will be in the less toxic (or non-toxic) trivalent form, and at typical discharge pH of $\delta - 10$ (mixed liquors) will be in a precipitated form. Under normal circumstances with recipient waters at pH circa 7.0 such chrome is unlikely to be redissolved. The effect of chromium on crops, which could relate to chromium in tannery effluent discharged to a stream subsequently employed for irrigation is covered briefly in earlier sub-section on solid wastes.

:- Sulphides

In addition to the noxious odour and unpleasant taste which can be imparted to recipient waters, the major effects of sulphide are :-

- decrease in dissolved oxygen (D.O.) content of waters, with possible effect on all forms of aquatic life;
- may cause dark coloured precipitates in presence of some metals (e.g. iron);
- toxicity to fish is increased as the pH value decreases. According to one report (14) trout overturned in two hours when 3.2 mg/litres of sodium sulphide was present in water at a pH value of 9.0. However, at pH 7.8 the trout overturned in 10 minutes, and at pH 6.0 it only required four

minutes to overturn the trout. Another study⁽¹⁵⁾ found that three species of fish i.e. Daphnia magna, carp and cambusia affinis could only tolerate a concentration of sulphide of 1.9, 50 and 760 mg/litres respectively; of far more importance is the toxicity to humans of hydrogen sulphide gas. In this respect it must be noted that if the pH of a sulphide bearing liquor is allowed to fall below pH 8.5 appreciable volumes of lethal H_2S gas will be discharged, with possibility of human fatality. This is unlikely to occur with tannery discharge to surface waters, but has caused fatalities in "on site" effluent treatment vessels holding lime liquors, and such potential danger would be greatly magnified if acidic liquors were admixed.

In addition to the hazards to humans raised by lethal H_2S gas in the confined space of sewers it may be noted that H_2S gas may condense on walls and be bacterially oxidised to form sulphuric acid, which may attack the fabric of such sewers. (Could have effect in internal tannery and municipal sewers).

:- "Organic". Load

The effect of the discharge of the general mixed wastes is very much a function of the level of dilution afforded by the recipient watercourse. The major effect of discharge of this "biological load" is noticed by its effectual lowering of the dissolved oxygen D.O. content of the recipient which could affect aerobic aquatic life. The earlier UNIDO/UNEP Study⁽¹⁾ making some assumptions^{*} as to the recipient streams reaeration constant calculated for a chrome tannery effluent :-

....."that to meet the water quality standard to support normal fish life a receiving stream should have at least a flow of 6 m³/day stream flow per kg of hide processed/day. At a lower flow of $4 \text{ m}^3/\text{day/kg}$ of hide processed/day the stream will not be able to support fish life in some of its reaches. At a still lower flow

*Note:

Sluggish stream, reacration constant 0.46, BOD removal 0.23 per day at 20° C with saturated D.O. value of 8 mg/litre.

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of 2 m³/day/kg of hide processed/day, the stream will be completely devoid of oxygen downstream of the waste outfall and the consequential anaerobic conditions may lead to the formation of floating sludge rafts, noxious gases, high turbidity etc., lowering the aesthetic value of the receiving waters".

Accepting this Paper's assumed water consumption of 45 litres/kg the above data may be calculated as necessary dilution factors for the stream to allow influx of the mixed tannery effluents :-

6 m³/day per kg hide processed=133 fold dilution - supports normal fish life
4 m³/day per kg hide processed= 89 fold dilution - localised degradation
2 m³/day per kg hide processed= 44 fold dilution - possible serious
degradation.

Such dilution factors may be a suitable base at which serious discussion between tanner and local authority may commence. It must be appreciated that the basic assumption employed in the calculation was that the recipient watercourse was not already heavily polluted upstream. Additionally, if there are other effluent discharges the effect of the total effluent discharges within the relevant stretch of waterway must be evaluated.

:- Miscellaneous

The above data concerning dilution refers to the "organic". load. The above Study⁽¹⁾ also made calculations regarding specific dilution requirements for tannery wastes to satisfy various beneficial uses of the recipient waters :-



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It is accepted that the above dilution factors are based on certain assumptions which will be dependent on local factors. In a perfect world an analysis of the relevant data would be carried out at each tannery site, however, in most Developing Countries facilities for such analysis do not exist and it is felt the above dilution data may provide basic guidelines.

CHAPTER III

IMPROVED ENVIRONMENTAL TANNERY PROCESSING

A STRATEGY

Tannery technologists are notoriously conservative and consequently reluctant to alter technologies which appear to yield a satisfactory end-product. However, with increasing pressure from local authorities regarding volume and cost of water consumed, levels of pollutant allowed and cost of effluent discharge, coupled with ever-increasing costs of chemicals, in many areas of the world, the industry is accepting adapted "improved environmental" technologies in order to offset such external pressures.

Whether or not all facets of "improved environmental processing" are installed within a particular tannery will depend on local circumstances and is still much influenced by external pressures. Thus, in arid areas, shortage of local water supplies may provoke a tannery process reappraisal, in other areas effluent discharge standards may be a greater stimulus to acceptance of more rational technology. However, as all aspects of "improved environmental" processing are interinvolved, it appears obvious that often a complete reappraisal of the whole operation is necessitated.

Thus if water volumes employed are significantly reduced (without any other process alteration) this would lead to smaller volume, but increased concentration of effluent, the effluent treatment costs (especially capital), would however, generally be greatly reduced. In some locations where the only constraints to effluent discharge are arbitrary local regulations relating to concentration of pollutant, such increase in concentration, due to lower water usage, would appear counterproductive, but should show the need for introduction of alternate innovative technology which will reduce pollutant discharge (lowered chemical offerings, recycling or possibly treatment of specific effluents).

An area where in-depth technical analysis of available technologies may be necessary is chrome tanning. Should one use the high fixation chrome systems (which may pose inflexibility in production) and in some cases ensure the final mixed effluent will conform to local discharge standards, or should one recycle (possibly more flexible in individual

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batch production, but not yielding a chrome-free effluent), or should one continue with existent tanning process but attempt to treat all liquors, with significant chromium contents, in order to remove chrome from the effluent.

An analysis of most tannery operations would suggest that with newer technologies financial savings may be considerable, and normally greatly offset any increased costs incurred by the need to increase levels of supervision to control such suggested innovative technologies.

Another consideration must be the level of effluent treatment thus if one ultimately intended a catalytic oxidation to remove sulphides, direct recycling of lime liquor may no longer be technically beneficial, but would justify an analysis of potential chemical savings, balanced against any loss or cost due to lowering quality of end-product and/or extra supervisory staff required.

Constraints on the introduction of "improved environmental processing" will exist due to existent tannery equipment and layout proving unsuitable, but given tanners normal ingenuity it should, in nearly all cases, prove possible to introduce updated technology within existing tanneries in the most critical areas :- reduction in sulphides, chrome and BOD load.

The introduction of extensive recycling of water may however, not be easily accomplished in a typical existent tannery, and indeed the conversion costs may not justify such action, whereas in a new tannery facility for recycling could, at relatively low cost, be considered. However, most tanneries given sufficient direction/pressure could find the means to recycle chrome liquors.

This Paper, directed towards Developing Countries, attempts to highlight the possibilities in these crucial areas, without the need for over-sophilicated technology.

B WATER CONSERVATION TECHNOLOGY

With variations in water consumption varying from $\langle 20 | / \text{kg}$ to $\rangle 100 | / \text{kg}$ for technologies apparently similar in other respects, there is in many situations scope for conservation and considerable savings in this area. The major systems of water-saving technologies may be :

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- Increased volume control of processing and "housekeeping" waters
- "Batch" versus "running water washes"
- Low float techniques in existent equipment
- Low float techniques using updated equipment (mixers)
- Recycling direct reuse of water to less critical processes
- Recycling of individual process liquors.

1. INCREASED CONTROL OF PROCESSING OF PROCESS AND "HOUSEKEEPING" WATERS

In a majority of tanneries only some 50% of water consumed is related to actual process requirement. The balance of the waters consumed appear to be due to extensive running water washes, overflowing vessels, continually running pipes and over-frequent washing of floors and drums.

Reduction of overuse in this area, while cost-effective, would necessitate a serious worker training programme, coupled with installation of water flow meters or less sophisticated spring controlled valves, and a written code of practice for operators (i.e. detail when floor, drum etc. needs hosing).

Considerable savings may be obtained with the introduction and control of simple "housekeeping" rules and equipment.

2. "BATCH" VERSUS "RUNNING WATER WASHES"

The age-old tannery system of running water rinsing, whereby goods are run in a drum with a lattice door with water valve fully open, for 15 - 20 minutes, is one of the major tannery wastages of water. Control of such process is minimal, neither the flow rate of water or the time, being monitored. Often such processes employ >1000% water, yet work at many research centres (16) (17) (18) (19) showed that 50% of total water could often be saved by instituting batch washes.

e.g. 1st Wash 250% water - 20 minutes Drain 2nd Wash 250% water - 20 minutes Drain

(Actual volume/time to be employed can be initially checked by testing pelt and liquor at various float/time levels).

Such batch washing should also yield a greater uniformity of product.
3. LOW FLOAT TECHNICQUES IN EXISTENT EQUIPMENT

The utilization of short floats, i.e. 40 - 80%, in traditional drums in place of traditional 100 - 250% floats, as well as yielding savings in water consumption and more rapid processing can, in many processes, effect appreciable volume of chemical input savings, due to the higher effective concentration and increased mechanical action.

Joint acceptance of both "batch washing" and "low floats" have been reported to save upwards of 70% of water utilized in tannery activity⁽¹⁷⁾. However, it must be noted that "low floats" may impose increased levels of "wear and tear" on the drum bodies and drive. The drive must be efficient to overcome the increased "inertia" at starting, and additionally, the increased temperature of goods in the drum, due to more friction and less coolant (especially during tannage), may not always be technically acceptable in tropical climates with high ambient temperatures.

With regard to water utilization it should be emphasized that where possible drums should be employed in place of paddles and pits which utilize 300 - 1000% floats. Although it must be recognised that paddles and pits are essential for certain processes i.e. first soaking of dried hides and processing of long-wooled skins.

4. LOW FLOAT TECHNIQUES USING UPDATED EQUIPMENT

The installation of hide processors (concrete mixers and Y partition units) is reported to yield water savings of 50% in addition to chemical savings. Such advantage is most unlikely, in existent tanneries in most L.D.Cs to justify import of these units at high foreign capital cost, when wooden drums may be constructed locally. However, in a new project such water and chemical conservancy coupled with greater general efficiency and regularity may justify the purchase of such units. The hide processors are ideally suited for, and require minimal civil works to allow recycling systems; most units incorporate efficient drainage systems.

5. RECYCLING - DIRECT REUSE OF WATERS TO LESS CRITICAL PROCESSES

In recent years a large number of proposals have been published showing that it is technically feasible to recycle many relatively clean

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rinse and wash waters to other processes where the low concentration of chemicals in such waste will have positive advantage (or at least minimal negative effect).

The simplest such proposal may be the Modified Bailey Process⁽¹⁾ outlined diagrammatically at Fig. IIIA. (The necessary pumps and holding tanks will be determined by the circumstances found at each tannery). Such system proposes that :-

(i) Wash after bate and neutralization and subsequent clean wash float are recycled to the soak process

(ii) Part of the second lime wash is recycled to form the basis for a new lime liquor.

Such Modified "Bailey" Process could reduce nominal water consumption from 17.1 litres/kg down to 12.6 litres/kg i.e. a reduction of some 26%. The engineering requirements of such system, while not being oversophisticated, may prove difficult in many existent tanneries, but could more easily be incorporated in a new project. The major requirement, in addition to collection sump(s) is the incorporation of a bifurcated drain whereby flow from any given drum could be directed either to :

(i) the recycling networks,

or (ii) normal effluent sewer.

Bifurcation of drain and collection system would <u>entail additional</u> <u>supervision</u> to ensure individual floats are discharged to correct outlet.

It may be agreed that the installation of a recycling network, merely to save some 25 - 50% of water usage, is unlikely to prove economic, except in ultra-arid areas where water is both limited and expensive.

But when simple water recycling is coupled with recycling of specific individual floats e.g. unhair and chrome, with savings in chemical offers the economies improve greatly, and must be seriously considered.

Slabbert of L.I.R.I.⁽²⁰⁾ outlined a recycling system which is shown at Fig. IIIB which incorporates :-

- (i) Recycling of used lime and post lime washes for soaking,
- (11) Recycling of pickle/chrome tan and some washes.

A reported advantage of this system is that the residual alkalinity, from the used lime float, acts as an accelerator for the soaking operation (20).

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The Slabbert system would appear suitable for many Developing Countries' tanneries. The details of the pickle/chrome recycling Slabbert outlines will be discussed at Chapter III E.

Figs. III C and D outline diagrammatically more detailed recycling systems :-

Komanowsky and Senske⁽²¹⁾ analyse a complete countercurrent system, as seen at Fig. III C. Conceptually such system has much to be recommended. This incorporates :-

(i) Simple reuse, without treatment, for some liquors

(ii) Chemical adjustment for other liquors (ammonia removal)

(iii) Certain physical treatment for a particular effluent (centrifuge).

The system of Komanowsky and Senske would drastically reduce the volume of effluent, as the complete pretanning process would only utilize one float. A visionary system in 1982, but potential for the future?

With regard to Developing Countries, it may be that such process would need unduly high levels of supervision, and certainly such a system would need to be practically proven at commercial level, elsewhere, for some years before such a radical proposal could be implemented.

Vulliermet⁽⁵⁾, at C.T.C. Lyon has detailed an "Optimum water recycling in soaking and unhairing", which is outlined at Fig. III D. Such system, separates the unhairing and liming processes and then recycles both simply (without treatment) and with treatment (protein separation). Technically Vulliermet's system has much to offer reducing volume of the effluent and lessening its total organic load,

but, as with the earlier Komanowsky and Senske system, will need proving at commercial level before it may be recommended for Developing Countries.

The engineering details of recycling must be adjusted to suit individual



tanneries, but in essence the most basic need is as outlined at Fig. IV. Whether or not a screen (static, bar, self-cleaning or brushed) is dependent on the liquor being handled. If screening is not included the pump must be protected (with a basket), and must be capable of coping with large and small fragments.

More detailed drum recycling equipment is outlined by Simoncini and de Simone⁽²²⁾ including screening at the drum and efficient means of continuous drum discharge.

6. RECYCLING OF INDIVIDUAL PROCESS LIQUORS

This will be outlined in later sections of this chapter under process headings.

C. LIMING AND UNHAIRING

Traditional soaking and unhairing account for over 80% of the B.O.D. and C.O.D. load in typical tannery effluents ⁽²³⁾ ⁽²⁴⁾. Accordingly there have been continuing researches to find new technologies to avoid this large pollutant load. Such researches have covered the following areas :-

- Substitution of sulphide
- Partial substitution and reduced amounts and volume of lime/sulphide
- Recycling without significant treatment of used bath
- More sophisticated systems.

During the now current "hair pulp" depilation process a high organic loading is obtained in the float due to the hair degradation products, often suspended in the float in a colloidal form. Attempts to revert to a "hair save" painting operation, which would yield a lesser organic load in the effluent, have generally been unsuccessful on hides due to In evaluating such enhanced labour costs (painting - unhairing etc.). processes it will be necessary to decide if they will give low-sulphide bearing liquors which will be acceptable to local authorities for discharge. Thus Frendrup⁽²⁶⁾ (27) recently reported that "...the use of proprietary unhairing systems had not continued to gain ground. If anything, the reverse was true, with Nordic tanners tending to favour classical unhairing systems", he also reported that beamhouse recycling was not found costbeneficial and sulphide liquors were ultimately catalytically aerated.

1. SUBSTITUTION FOR TRADITIONAL SULPHIDE UNHAIRING

Most of the major chemical supply houses have been engaged in the search for an economic, technically acceptable replacement for lime/ sulphide depilation and "liming". Di-methyleamine sulphate, sodium chlorite, sodium bichromate, mercaptans and enzymes amongst others have However in general the results have not proved been investigated. (29), after a Survey, acceptable, Frendrup reported pollution levels from differing systems. (See Table V). The usual reaction of tanners has been that the cost is prohibitive, or short hairs were remaining, necessitating further mechanical or chemical processing. One recent Paper⁽²⁸⁾ found that the enzymes were not specific, yielding some damage to the grain structure.

<u>TABLE V</u>	AMOUNTS OF POLLUTION ARISING FROM VARIOUS UNHAIRING SYSTEMS (Expressed as g/kg Raw Hide) (POLLUTION FROM UNHAIRING ONLY)					
	HAIR F	ULPING		HAIR SAVING		
	LIME SULPHIDE	NaOH NaSH	OXIDATIVE (C10 ₂)	LIME SULPHIDE	DIMETHYL AMINE (D.M.A.)	ENZMO
S.S.	45	14	14	28	24	
B.O.D.5	25	29	11	5.5	6.6	14
C.O.D. (K ₂ Cr ₂ 0 ₇)	70	100	40		20	34
S	6.5	7.5	0	0-3	0-18	0.3

Certainly, on a semi-experimental basis, enzyme and other systems have proven efficient. Ludvik (25) reported on an acceptable enzymatic depilation in Czechoslavakia (however the enzyme is no longer available).

With regard to commercial exploitation and proving trials, it would appear that there are possibly only one or two tanneries in the world with complete lime/sulphide substitution, a few more tanneries employ enzymes followed by a lower level lime/sulphide treatment. Thus such systems may not be developed sufficiently to be suitable for installation in tanneries in Developing Countries. It must be noted that even

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sulphide-free unhairing systems yield some sulphide in the effluent, reported as 10 - 50 mg/litre, due to the breakdown of the disulphide bonds within the hair keratin.

2 PARTIAL SUBSTITUTION, REDUCED AMOUNTS AND VOLUMES OF LIME/SULPHIDE

The use of sulphide and caustic soda, which while still containing sulphide should have lesser suspended solids in the effluent, is in current practice - the major problem of such a system is the need for strict control of the caustic soda, as minor variations are reflected in large variations in swelling and plumping of the pelt (whereas with lime, the low solubility acts as a self-regulator).

Prentiss⁽³⁰⁾, Sukach⁽³¹⁾ and Fritz⁽³²⁾ amongst others have recently proposed processes with limited inputs of lime/sulphide augmented by proprietary products (some enzymatic).

van Vlimmerien⁽²⁴⁾ and co-workers at T.N.O. believing that calcium ions imparted some essential characteristics during beamhouse processing, proposed a two-stage process :-

Soak

100% water

1% Calcium Chloride 0.4% Magnesium Oxide

Followed by :

Unhair

30% water 1.8% Sodium Sulphide 0.8% Sodium Hydroxide

Gaughhofer⁽³³⁾ describing the results of a full scale trial in Switzerland found the T.N.O. system encouraging, but expressed some doubt as to the processes applicability if light, soft leathers were required.

Currently, few of these partial substitution lime/unhairing systems have been fully accepted for commercial production - they are utilized in a few tanneries in Developed Countries, but usually only when local effluent discharge regulations have been over-severe. Many tanneries have attempted these substitution processes, but for technical or economic reasons have umually reverted to a more classical process, in association with a subsequent sulphide removal treatment. On balance, a minimum recommendation to tanneries in Developing Countries must be to reduce chemical inputs of lime/sulphide to the minimum - approaching:-

Drum process:- 200% water 1.5% lime 0.8 - 0.9% S (i.e. 2.5% Na₂S (60%) plus 0.5% NaSH (90%))

3 RECYCLING OF CLASSICAL LIME/SULPHIDE LIQUORS

During the last decade the possibilities of direct recycling of lime/sulphide liquors has been widely examined. Frendrup⁽³⁵⁾ reported a system whereby liquors were mended, the initial liquor was :-

```
300% water
5% lime
4% Na<sub>2</sub>S (60%)
```

Following each batch the liquor was mended and each pack cycle consumed :-

```
70% water
1.7% lime
3.0% Na<sub>2</sub>S
```

Such mending trials were said to have run 14 cycles with no adverse effects on the leather noted. Others (33) however report a significant reduction in the thickness of the limed pelt.

Money and Adminis⁽³⁶⁾ at C.S.I.R.O. Australia, reported on similar work using an initial float of :-

```
200% water
2% lime
4% sodium sulphide
```

mending after each pack required :-

1.5% lime

2.2% sodium sulphide

with water being replenished to original levels. Water replenishment was from 40 - 55% - the higher levels occuring when solids were screened off prior to liquor reuse. (Most workers in this field report many advantages in screening (1 mm. mesh) to remove solids and hair debris. Brushed, stainless steel screens seem most suitable for this function, see Chapter IV). Prima facie, such recycling systems would appear to offer effluentfree unhairing if continued ad infinitum, however, this may be an oversimplification. With every batch of goods large quantities of hair and other proteinaceous products are destroyed and retained within the effluent, much in colloidal form. It could have been expected that recycling would result in ever-increasing concentrations of protein decomposition products building-up in the liquor until equilibrium was established, with high levels of organic load being expelled with insterstitial liquors at the fleshing machine and during deliming and later processes (with high B.O.D. load entering the effluent).

If such higher B.O.D. loads were produced at deliming and later processes, it would be counterproductive, as pollution would, being more dispersed, be harder and more expensive to treat. However, Money and Adminis found in their trials" that recycling of lime liquors will not greatly increase the protein content of later processing liquors." They concluded that"some protein, or its degradation products, must be retained or taken up by the hide whenever a liquor is reused."

The C.S.I.R.O. work concluded that the hides, following recycling of lime liquor, were not as free of scud as when treated in fresh liquors, but felt this could be remedied in later processes without mechanical scudding. Fat build-up may also occur (unlikely to be too great a problem in hides in most Developing Countries, as their hide fat levels are low), this was reportedly eased if screening was practised prior to recycle/mending.

Slabbert⁽²⁰⁾ more recently reported on similar recycling trials employing 3% Na₂S (60 - 62% pure)

2% lime

found chemical savings of:

> 20% of the normal sulphide 40% of the lime.

Whereas work at C.T.C. Lyon⁽¹¹⁾ suggests savings of : 50% sodium sulphide 60% lime

"....related to quantities theoretically required, and calculated over 20 cycles".

Slabbert indicated that high levels of sodium chloride, possibly present from brine cured rawstock, could have inhibiting effect on

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unhairing and scud removal. This may be avoided by giving adequate soaking/washing.

Some degree of analysis and control is certainly essential when a recycling system is being installed. In Developing Countries where works control laboratories and staff are not always available, it could prove practical in such circumstances to employ an external chemist for, say, 2 - 4 weeks to aid in implementation of the system of recycling. Equilibrium is established after 5 - 6 cycles, "mending" requirements could be controlled by analysis for a week or two and when relative stability achieved and mending requirements assessed, recycling could be practised with only intermittent analysis.

Aloy⁽³³⁾, C.T.C. Lyon, reported that employing a recycling system, incorporating only a vibratory screen (1 mm. mesh), a French tannery with an input of 25 tons raw hide per day effected savings of F.Frs. 11,000 per month! (i.e. tannery with approximately 1,000 hides per day could obtain savings of U.S.\$ 8,000 per annum).

If recycling is instituted it would still be necessary, in a tannery, to have facility to process such used lime liquors. Although recycling in theory may be continued indefinitely, occasionally it may be necessary to discharge a liquor, during a holiday shutdown, or if the liquor has been contaminated. Thus a back-up system of catalytic oxidation (see Chapter IV) or similar should be available.

4. MORE SOPHISTICATED SYSTEMS OF RECYCLING

A wide range of recycling techniques exist to minimise both sulphide and organic load in beamhouse effluents. In general they may currently be assumed to be too sophisticated for tanneries in most L.D.Cs and thus here they are only noted :-

a) <u>Sulphide Stripping</u> is practised in many tanneries - the liquors are acidified and the H₂S gas released, collected in a caustic soda solution prior to subsequent reuse. (Requires high level of plant control to ensure no escape of toxic gas).

b) <u>Protein Precipitation</u> has been suggested as a means of lowering pollutant level of beamhouse effluent. Would require a method of sulphide removal (catalytic oxidation) followed by acidification. Subsequent liquor could be recycled to wash or delime baths. (See Fig. III D earlier) (Vulliermet⁽⁵⁾, Schubert & Pauckner⁽³⁷⁾.) c) <u>Ultrafiltration</u> Several of the proprietary recycling and effluent treatment systems employ ultrafiltration to separate the spent depilatory float. In essence the system is :-

Following a fine mechanical screening the used lime/sulphide liquor is subjected to ultrafiltration, employing a pump, and a series of membranes in an ultrafiltration cell. The membrane separates the spent liquor into :-

(i) solution containing the dissolved lime and sulphide and other salts, together with some part of the protein degradation products (those broken down sufficiently to pass through the membrane).

(ii) a concentrated sludge/slurry containing the undissolved lime and the bulk of protein materials.

The solution, following analysis, may be mended and recycled to a new time siquor, and the sludge may be further treated prior to dispose.

Currently altrafiltration equipment is highly expensive, however, if as appears likely, such units gain acceptance in Developed dountries! tanneries, it may be expected that their cost will be reduced, and their reliability improved, at which time they may be generally suitable for employment in Developing Countries! tanneries.

D. CHROME TANNING

1. BACKGROUND

It has been long accepted that the majority of chrome tanning technologie. are somewhat inefficient, due to the low levels of chrome fixed from the tanning bath, coupled with "bleeding out" of chrome in subsequent processes.

Whether trivalent chronium in effluent and sludge has a serious toxic effect becomes somewhat academic as in many countries very low levels of chronium are allowed to be discharged. Accepting this situation is becomes imperative for tanners to evaluate their current situation and decide how to minimise their chronium discharges. Research, directed towards minimising discharge of chrome in recent years, has covered the three major areas :-

High Chrome Fixation Techniques have been developed, generally employing additions of dicarboxylic acids, which can yield up to 99% fixation of chrome offer with concomitant low levels of chrome in effluent.

<u>Recycling</u>, used chrome float recycled to form basis of next tan bath or pickle bath.

<u>Precipitation</u> - chrome bearing liquors are collected, treated with an alkali to precipitate chromium hydroxide which, when separated from the supernatant, may be redissolved for use (or even discarded to controlled dumping site).

The consultant believes that each of the three techniques is technically feasible, yields great economic advantage and lower levels of pollutant, <u>has</u> been commercially proven and accepted, and may be recommended. Tanners must evaluate the most suitable technique, given their particular circumstances.

2. HIGH CHROME FIXATION TECHNIQUES

Typical chrome fixation levels are quoted in a recent B.L.M.R.A. Study by Covington⁽³⁹⁾, who prepared chrome balances for some 72 different packs of leather at 12 U.K. tanneries. He reported wide discrepancies in chrome fixation. These are summarised in Table VI.

	TABLE VI	CHROME	BALANC	ES (From	Covingto	n ⁽³⁹⁾)
Percentage of Chrome Offer in :-	Bovine T	anneries	<u>Ovine</u>	Tanneries	Leather	Dressers
Leather Spent Tan Liquor Samm Liquor Drain Liquor	55 34 8	to 79 14 5	48 27	to 95 1	52 41	78 25
Post Chrome Liquor			24	1	6	
TOTAL	99	99	99	97	99	103

The data in Table VI certainly supports the viewpoint that current

chrome tanning technology is often inefficient from the economic viewpoint and confirms that high levels of chromium may enter effluent from both the "spent" tan float and subsequent processes.

Tanners are aware that chrome fixation is favoured by :-

Short float Increased temperature Increased time of tanning Increased basification Decrease in neutral salts

Employing these techniques it is possible to raise apparent chromium fixation levels to 80 - 85%, but the unutilized chrome is still at far too high a level to satisfy discharge limits often imposed. Additionally the leather will be holding interstitial liquors containing unfixed chrome, which will bleed out in subsequent processes (sammying, neutralizing etc.), revealing real chrome fixation levels lower than quoted above.

Recent work, some patented, directed towards higher levels of chrome fixation has concerned the incorporation of dicarboxylic acids and their salts (aliphatic 4 - 6 c. atoms e.g. adipic and aromatic materials e.g. phtalic), into the chrome tannage. Such materials had traditionally been introduced into pickle and chrome tanning processes as masking agents. Luck⁽³⁸⁾ reports on the efficiency of a new system employing the dicarboxylic material as a second phase addition to a chrome tanning process. The process, following a short pickle, is commenced with a low offer of conventional 33% basic chrome tanning salt and completed with addition of self-basifying chrome tanning compound and dicarboxylic acid.

Luck (38) suggests a drum formulation for "particularly good exhaustion" is :-

<u>Pickle</u>	10 - 5	\$0 %	water at 20°C
		0.25%	sulphuric acid
		0 •6%	formic acid
	3 -	6 %	cormon salt
			1 hour
Tan		0.8%	Cr ₂ 0 ₃ of 33% Basic Chrome tanning salt

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1 hour

	add	0-7%	Cr ₂ 0 ₃ self basifying tanning salt
	add	1•6 %	mole dicarboxylic acid/mole $22_{20_3}^{0}$
	Run 7.5 hou	rs – en	d рН 3·9 - 40 ⁰ С.
Alte	rnatively, i	n pract	ice, Luck for hides suggests :-
Pick	<u>le</u> .	20 %	water
		3%	salt
		0-8%	sulphuric acid
			1 ¹ / ₂ hours pH 2·7
Tan	add	4-1%	chrome tanning salt 33% basic 26% $\text{Cr}_2^0_3$
	Run 3.5 hour	rs pH (2 • 8
	Add	1•8% p	atent self basifying organically masked
		c 2	hrome tanning salt 20% 7:0 (e.g. Baychrom 403)
	Run 8 hours	s 4	9 – 50 [°] C
	Leave in dr	um overm	night nH l+0

Such process is said to yield only some $0.7 \text{ g/litre } \text{Cr}_20_3$ in the residual float. Somewhat similar high chrome fixation is claimed by BASF employing "Impenal DC" and Messrs Rohm propose the employment of a "chrome exhaust aid chemical".

Luck, arguing in favour of the "high chrome fixation" operations versus the efficiences of recycling systems (See III D 3 later) suggests that the major advantage of "high fixation" is that "bleeding out" of unfixed chrome from hide (and any splits) in later processes is greatly minimised, as well as the more economic usage of chromium. Luck's Paper⁽³⁸⁾ analyses chrome content of the residual tanning bath and subsequent processes, employing a typical recycling system in comparison with a "good exhaustion process", employing as an example hides together with their split, and reports as can be seen at Table VII.

Luck further draws up a chrome balance for the two tannage systems which may be seen summarised at Table VIII.

Certainly, on the evidence of Table VIII the High Chrome Fixation system would appear to offer a 75% further reduction of chrome in discharges, (effluent and solid waste, according to treatment system employed) over a recycling system.

TABLE VII CHROME OXID	E CONTENTS C	OF FLOATS (As Luck ⁽³⁸⁾)			
(g/litre Cr ₂ 0 ₃)					
Process	Recycle	"Good Exhaustion"			
Residual Tan Float Retan Float Wash Float Fat Liquor Float	6+4 0+94 0+20 0+20	0·7 0·15 0·08 0·08			
Split 1st Wash Float Split 2nd Wash Float 3rd Wash Float	0·71 0·43 0·23	0·18 0·08 C·05			

TABLE VIII C	HROME BALANCE: - RECY	CLE versus GOC	D EXHAUSTION
	(Calcul	ated in kg Cr ₂	03/tonne pelt
MATERIALS EMPLOYED		RECYCLE	PROCESS WITH WOOD EXHAUSTION
	Recycle New Material	4·4 16·0	14.3
	Total Employed	20.4	14.3
In leather after t	anning 16.0	14.	08
Residual Tan Float Ex Liquors pile, s Ex Retan residual Possible leechings	amm, split float from splits/shavings	(4・40) 1・30 1・08 0・81	0·22 0·14 0·24 0·18
Total Unus	ed Chrome	3•19 kg C	^{cr} 2 ⁰ 3 ^{0.78} kg ^{Cr} 2 ⁰ 3

However, a caveat may be entered to point out that such proprietary processes, as are available today, may not be 100% suitable for all productions. Some tanners in Developing Countries have reported difficulty obtaining the high final temperatures required, possibly due to the small size of drums employed, with concomitant lesser levels of mechanical action. The converse has also been reported, in areas of high ambient temperature, difficulty has been experienced in keeping below the suggested temperature levels. It is reported that some high exhaust systems cannot cope with heavy hides, and in general, are not suitable in circumstances where a variety of tannages are employed to obtain variations in feel, softness etc. Thus if processing skins or light and medium hides, with a few standard processes only, the proprietary "good exhaust" process may be recommended to yield lesser concentrations of Cr_2O_3 in effluent. The savings in chrome offer would more than offset the increased costs of the patent materials.

3. RECYCLING

Traditionally pickling and chrome tannage ere carried out in separate floats. Today however, in most tanneries, short nonequilibrium pickles to which chrome tan is later added, appear most usual. Paddle pickling is however still often current practice in the processing of skins, and thus this simple form of possible recycling should be noted.

a) <u>Pickling</u>

An initial pickle liquor of :-

500% water

50% salt

5% sulphuric acid

could be tested before and after use (when volume restored to original) using hydrometer for salt and simple titration for acid. It could be found that

	Initial Float	Used Float	Mending Requirement	
Water	100活	70 - 80%	Restore to original	level
Salt	10%	9%	1%	
Sulphuric Acid	1%	0.8%	0.2%	

The necessary chemical additions to restore the liquor to original strength may easily be calculated.

Such simple pickle regeneration - well within all tanners technological control - although not having a significant effect on major toxic materials in effluents can by reducing the salinity of tannery effluent prove environmentally acceptable, especially in such areas where tanneries discharge to surface waters and downstream such waters are utilized for domestic and agricultural purposes, where salinity has negative environmental effect. The advantages of saving of chemical offer are self-evident.

b) Chrome Tannage Recycle

The concept of recycling of used chrome tanning liquors was felt for long to be fraught with danger, as it was feared that of the many differing chrome complexes known to exist in the chrome tanning materials employed, some would be differentially taken up by the pelt leaving a residue of certain other complexes and other constituents which would build up in the liquor on recycling. Such differential uptake, it was felt, would lead to ever differing characteristics of leather from recycled liquors. The work at C.S.I.R.O. Australia, published in the '70's showed this was not so, and that for all practical purposes uptake of chromium complexes was effected equally.

In 1973 Davis and Scroggie published a now classical series of Papers (40 - 44) covering laboratory and tannery trials of chromium Their Papers initially detailed a recycling system liquor recycling. suitable for use with an overnight equilibrium pickle⁽⁴²⁾, the used chrome liquor following screening was "mended" prior to use for the Later they published details⁽⁴³⁾ of a recycling process next pack. suitable for employment with short duration non-equilibrium pickles, whereby the used chrome liquor was recycled to become a pickle liquor This system seems most likely to find for a subsequent pack. commercial acceptance. The C.S.I.R.O. workers published (45) a later Paper based on tannery trials outlining the general requirements and problems of chrome liquor recycling. More recently B.L.M.R.A. workers studied and reported (46) on tannery chrome liquor recycling systems in actual use and their efficiencies. The essence of these processes is outlined below :-

(i) Recycling of Used Chrome Liquors (to tannage)

One of the major problems of simple recycling systems is the low efficiency and erratic drainage of most drums in use. Thus, a supposed "drained" pickled pelt pack in a drum could well be holding some 20% residual float. Whereas after tanning the leather is removed from the drum and allowed to drain, while being horsed for 18 hours, thus each cycle will have at its disposal: all the tan float plus, say, 20% of pickle carry over float, together with float introduced with chrome liquor and basification additions. Evidently such increasing volume cannot be recycled and this system of direct recycling may only be partial. In other tannery situations facilities do not exist to recover into the collection system all of the float which is discharged with the tanned goods. Thus again allowing only partial recycling.

Fig. V below shows an outline of a typical basic recycle trial from one of the B.L.M.R.A. tannery case studies. Brief perusal of the "original" viz-a-viz the "recycled" process should enable a technologist to appreciate the essentials. In each tannery the basic parameters must be determined by measurement and analysis (chrome content of liquor would initially require chemical analysis - once a system is operationally stabilized colorimetric methods of analysis could be suitable).



From Fig. V it may be seen that recycling was at the level of 57%. This was reportedly due to the loss of 43% of liquors at the tannery, while the hides were being discharged from the drum. Given more efficient liquor collection higher levels of recycle may be effected, remembering, as noted above, the inability to recycle 100% float. Such 57% recycling may be a typical level of achievement in an existent tannery where makeshift engineering work has been employed to allow such recycling. Given a new plant more efficient drainage and collection systems could raise the recycle level to $\frac{1}{2}$ 80% of total float discharged.

The recycle system shown at Fig. V would effect :-

a 24% reduction of new chrome offer

a 57% reduction of chrome discharged.

(ii) <u>Recycling Used Chrome Liquors to Pickle</u>

The process detailed by Davis and Scroggie (44) (45) was :-

<u>Initial pack</u>	60%	water
	6 %	salt Drum at 13 r.p.m. for 10 minutes
Add	1.6%	sulphuric acid (65%)
	0•35%	formic acid (85%) Drum 110 minutes
Add	2•25%	Cr ₂ 0 ₃ (Sugar reduced 38% basic)

Drum 7 hours

Basify with soda ash in two stages over 4 hours

The spent chrome liquor was then discharged from the drum run into a storage vessel via a coarse wire mesh screen. Analysis of chrome, salt etc. was then carried out.

Subsequent packs

"The residual chrome liquor from the preceding run, after additions of sulphuric and formic acids" was used to provide a new pickle float :-

1.65% sulphuric acid (65%)

0.28% formic acid $(85\%)^{**}$ were added, after running two hours the calculated reduced chrome offer was given (following analysis of recycled bath)." Davis and Scroggie reported recycling over 80% of the used bath and found in their trials, chrome needed was 78% of original offer.

Sharp⁽⁴⁷⁾ described a recycling system in practice where spent chrome liquor is pumped from hide processor, via a self-cleaning screen, then to a storage tank for cooling. Some two-thirds of the float is recycled, the balance discharged to effluent sewer. He emphasized that when the system was installed in 1975 it was based on economic advantage not environmental considerations.

Acid required for mending will be dependent on levels of basification employed during tannage.

The reduction in offer of formic acid was to avoid a build-up of formate ion concentration or highly masked chromium complexes in recycled liquors.

Arnoldi and Covington⁽⁴⁶⁾ studying processes employed in U.K. tanneries found 70% of float recycle possible with 25% savings of chrome offer as may be seen in Fig. VI.



Even with the 70% reduction in discharge of chrome to the effluent the B.L.M.R.A. workers suggested the contribution to chrome in the effluent of such recycled process was 55 mg/litre Cr (111).

One further advantage of recycling spent chrome liquors to the pickle process is that salinity in the effluent is greatly reduced.

The principle of employing a liquor containing chromium as the pickle float is that, given normal conditions, the acid and salt from such liquor penetrate the hide faster than the larger chrome complexes, thus the pelt should be neither swollen or over-reactive when the chrome contacts the pels.

Note regarding operation of recycling systems

Employing the process outlined above there will be a significant alteration in concentration of neutral salts. Initially the residual chrome liquor will contain high <u>chloride</u> content (from the common salt pickle), this will decline during the recycling process, and be replaced with <u>sulphate</u> entering the system as a constituent of the chrome tanning salt.



Slabbert at L.I.R.I.⁽²⁰⁾ confirmed the change in neutral salts concentration (see Fig. VII) and reported savings of 15 - 20% chrome tanning agent, in addition to 100% of common salt.

Is mentioned earlier the ideal situation would be where provision was made to collect all spent chrome - from tan bath, hides being hauled, drainings from horsing and sammying and later processes.

However, in most tanneries such is not possible without complete re-engineering. In most situations one must endeavour to collect the significant volumes, at minimum main float draining and sammying liquors so as to justify the extra controls required, and earn sufficient of the rewards of lesser chemical inputs.

Recycling requires some regular control and monitoring; initially most liquors require analysis. Once the system has stabilized, control may be generally by way of simple tests, with only occasional need for full analysis. The pH and specific gravity will give guidance as to the acidity and salt content.

Some of the problems associated with recycling are discussed by the C.S.I.R.O. workers ⁽⁴⁵⁾, they suggest that some minor acid swelling could occur during pickling and tanning if improperly controlled, due to incorrect salt concentrations. They suggest that "....control of salt concentration in the recycled liquor at a level which restricts the swelling of the pelt to the same level

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as in a normal process is critical", deviation from such correct salt concentration may be due to :-

:- poor drainage of the pelt prior to entry of pickle liquor may cause overdilution of salts present. (If drainage not controllable may adjust salt content by addition of sodium chloride 1 - 2% following tests of specific gravity).

:- chrome tanning product employed may contain insufficient sodium sulphate to keep total neutral salts at safe level to repress swelling. Propriétary chrome tanning products vary in sodium sulphate content from 3 - 30%. (Davis and Scroggie in their work utilized a product containing 24% Na₂SO₄ and with this automatic neutral salt addition found the neutral salt balance easy to maintain.) (The B.L.M.R.A. process study⁽⁴⁶⁾, outlined at Fig. VI possibly utilized chrome products with lesser sodium sulphate content, necessitating the cyclic "mending" with common salt).

:- for recycling floats of 70 - 100% were recommended, employment of ultra low floats, e.g. 30% for recycling were felt to raise problems as the addition of liquid chrome offer and dissolved basification additions could have serious dilution effect on the neutral salt content.

NOTE: The mending of pickle/chrome liquors is possibly best accomplished in a holding pit so that at the contact of pelt/ liquor a normal safe salt concentration is available to avoid swelling. If it is wished to prepare the liquor in the drum normal precoutions must be taken to first add the salt.

(iii) Recycle of Chrome Liquors - Precipitation

The two systems of liquor recycling outlined above will necessitate the technologist altering, to a considerable extent, his technology as well as civil engineering works. An alternate approach requiring little adjustment of technology is to continue with a normal chrome tannages- Collect maximum volume of substantially chrome bearing liquors. (Float, drainings, sammying extractions and possibly any preneutralization wash). The isolated chrome bearing liquors are treated with an alkali to precipitate the chromium in the hydroxide form. From this point there are two possible means to utilize the chrome :-

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:- The hydroxide sludge may be passed to a filter press, the cake so formed may then be redissolved with sulphuric acid and reused.

:- The liquor may be left undisturbed overnight, virtually "chrome free" supernatant may then be drawn off and discharged to the effluent stream and the remaining settled hydroxide sludge may be redissolved with acid in situ and subsequently reused. A schematic outline of the process may be seen at Fig. VIII.



NOTE: 1 Ref: Precipitation of Chrome from Spent Liquors

The alkali utilized for precipitating the chrome in spent liquors may be dependent on the subsequent recycle system. Constantin and Stockman⁽⁴⁸⁾ found that hydrated lime was "the most effective precipitating agent" such "lime precipitated chromium hydroxide reacted favourably with flocculants to form a large, sturdy, settleable floc. They also found "an anionic polyelectrolyte, Nalcolyte 677 (NALCO Chemical Co.) was optimum at 20 - 30 p.p.m." This work appears to have been directed towards ease and efficiency of treatment in a filter press.

<u>NOTE: 2</u> - As the employment of expensive filter presses does not appear essential this Paper, directed towards Developing Countries, will concentrate on the alternate technique of redissolving the sludge.

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T.N.O. workers however reported $^{(49)}$ that"Magnesium oxide turned out to be the most attractive precipitant, giving compact precipitates (10% $\text{Cr}_2^{0}_3$ in wet precipitate), a high sedimentation velocity (0.25 m/h)" ... together with low residual concentrations of chromium in the supernatant liquor (5 mg/l).

A more recent paper by workers from T.N.O.⁽⁵⁰⁾ again recommended magnesium oxide as the precipitating agent, when there was to be in situ separation by decantation. They suggest that comparable results may be obtained employing sodium hydroxide but the additions need to be added slowly - over 10 hours.

As a large excess of magnesium oxide is required to reach the optimum pH of 8.5 they suggest that the most effective method is to precipitate the first 80 - 90% of chrome employing magnesium oxide. This is followed by slow addition (over one hour) of The T.N.O. system is outlined ⁽⁵⁰⁾:sodium hydroxide solution. ".....The chrome bearing liquors are passed through a grating to remove coarse insoluble material and collected in a pit, kaolin is added (1 kg/m³) and the suspension mixed and pumped to a sedimentator (Dortmund Tank - see Chapter IV), here the fat and fibres present rapidly settle with the kaolin and the clear supernatant may be drawn off to a treatment tank. 80 -90% of the theoretical amount of magnesium oxide is added as a 50% aqueous suspension. After one hour stirring sodium hydroxide is added slowly to pH 8.5. Then the suspension is left to rest overnight with a view to settling the chromium hydroxide. Next morning the supernatant liquor which is nearly free (\sim 2 g Cr/m³) of dissolved chromium is drained through a decantation pipe."..... "As soon as the quantity of precipitate is so large that there is no room left for a new charge of chrome liquor, the precipitate is dissolved in sulphuric acid. Because of the production of heat of hydration and neutralization, cooling is essential. After dissolving the chrome liquor is diluted to the calculated volume and transferred into a storage tank to be recycled to the tanning process".... "The amount of sulphuric acid which is needed, as well as the end volume of the chrome liquor, are directly proportional to the amount of magnesium oxide and sodium hydroxide used for precipitation."

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The clarification sub-process employing kaolin may well achieve superior results, however, it does entail a sedimentation vessel to be specially constructed and technically acceptable results have been reported without such clarification.

The use of a patent form of magnesium silicate as a clarifier during chrome recycling is reported (51) to give good results at the Wolverine Tannery in the U.S.A. Such process could be carried out without a sedimentation tank - just employing pump-over of supernatant liquor into another pit.

The proposers of the high chrome fixation processes NOTE: discussed earlier suggest that the major advantage is that the post tanning spent baths contain low levels of chrome. However, Langerwerf and Pelckmans⁽⁵⁰⁾ suggest that "high chrome fixation" processes can still yield over 200 g/m^3 chrome due to suspended The system of precipitation and settlement fibres containing chrome. of used chrome liquors, outlined above, would eradicate such chrome from the major chrome bearing liquors. They suggest that the retan and other chrome bearing liquors may be treated to a special chrome flow sedimentation treatment to yield a clarified liquor of low Cr₂0₃content. (See Chapter IV).

NOTE: 4 - Employing the low installation cost of precipitation, removal of supernatant and direct in situ dissolving of chromium, van Vlimmeren in 1979 calculated savings for a daily input of 25 tonnes W/S hide :-

 Value of recovered chrome p.a.
 D.M. 232,000

 LESS
 Cost of chemicals
 D.M. 37,000

 Labour (1 man)
 D.M. 29,000
 66,000

NET SAVING

D.M. 166,000

Thus at 1979 prices in a tannery processing approximately 1,000 hides a day, annual savings of D.M. 166,000 (approximately U.S.\$ 70,000 per annum) could be directly achieved.

In the European context where effluent charges relate to strength of constituents, the savings due to chrome removal would be five or six times the above amount. Higher levels of savings

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could be expected in Developing Countries due to higher cost of chromium and lower labour costs.

E VEGETABLE TANNAGE

Although vegetable tannages have declined in importance in recent years, there is still a wide general usage of both complete vegetable tannage and mixed chrome/vegetable, vegetable/chrome and vegetable/syntan for certain end-uses, and in several geographic areas vegetable tannage is the major process employed by domestic tanners.

With regard to effluent, vegetable tannins have been stigmatised due to their possibility of forming dark coloured precipitates, when in contact with metals and their resistance to biological breakdown. However, in mitigation, it must be recognised that they have not created undue adverse criticism, as they are naturally occuring products (albeit concentrated for tannery usage).

The traditional countercurrent pit systems were to some extent self-regulatory with regard to effluent characteristics, as when liquors were discharged they were almost spent of tannins. The more recent attempts to speed up processing employing higher concentrations of tannins in drums have possibly led in some cases to more concentrated effluent discharges.

Due possibly to the decline in importance of vegetable tannage, limited research work only appears recently to have been expended in elaborating vegetable tannage processes with minimal effluent. In the field of sole leather tannage the L.I.R.I. process is now universally accepted as the basis for a virtual "no effluent" process. Although even with the Liritan system minimal levels of tannins may enter the effluent from post tan washing and filling operations, such concentrations will be far lower than would be obtained when actual tan floats were discharged.

1. SOLE LEATHER

Shuttleworth⁽⁵²⁾ and others have described the Liritan "no effluent" system of sole leather tannage. The system proposed and proven in practice, is to condition the hides so that they may be ontered into a high strength tan bath, allowing rapid penetration and fixation without overtanning the grain layer, this is followed by tannage in a closed circuit of controlled pits.

a) Conditioning

Is carried out following deliming, employing a mended bath in pit or paddle for up to one day

Original Condition Bath:- 5% polymeric polyphosphate 2% sulphuric acid

When goods are removed the liquor is mended with :-

2.5% polyphosphate

1.25% sulphuric acid

and is ready for the next batch.

b) Tannage

The conditioned hides are suspended in the last of a series of pits (6 - 10), daily or otherwise moved up the series. The time of tannage may be 2 - 6 days according to substance. pH is held at circa 3.5 constant temperature = 35° C, liquor is kept at 100° BK (13.1 Baume), and liquor circulated around the circuit so as to change every 4 - 6 hours.

The process is shown diagrammatically at Fig. IX.

The concentration of tannins is kept constant by additions to the mending pit - extract may be suspended in sacks to allow slow augmentation.



Following a wash the goods may be filled etc. as required. Some tannin will be present in the wash liquor, part of which could be used to recharge the level of the system to replace lost liquor withdrawn with the goods.

Similar closed circuit "no effluent" tannage systems have been proposed employing syntans as "conditioners", these may not be as economic as the LIRI system, but could yield equally low concentration of tannin in the effluents.

KIP PROCESS 2.

No commercially 100% effluent-free light vegetable tannage has A low concentration of tannin in a Liritan yet been developed. type circuit could possibly reduce tannin in effluents, but such process Of the current processes a minimal may be unduly lengthy in time. discharge of tannins could be obtained from a short float rapid drum process, as proposed by Atkinson and Scowercroft⁽⁵³⁾. Following delime and bate :-

Light Pickle	60%	water				
	6%	salt				
	0.6%	sulphu	ric acid	1		
Drum unt	il penetra	ted and	equilit	orium	rea	iched
			1		-	

0.25% Cr₂0₃ (1% commercial chrome tan salt) Condition Add

Drum until fixed

Drain heavily

Main Tannage

Add to the hides in drum without float

Spray dried Mimosa Extract 6% Run $\frac{1}{2}$ hour Spray dried Mimosa Extract 9% Run 1 hour water at 35° C. Run 2 hours 25% Drain. Spray dried Acidified Mimosa Extract 5% Run until penetrated, approximately 5 - 8 hours, depending upon average weight of the skins Wash Bleach Oil etc.

To minimise pollutants in effluent, the 30% float on horsing up draining could be recovered and reused in lieu of the tan/water addition for the next pack.

Such process could be applicable to other spray dried tannins and is suitable for skins and light/medium hides with tan offer being adjusted to suit hide substance and end-product.

F. COSTS OF INTRODUCTION OF RECYCLING AND OTHER TECHNOLOGIES

With the wide disparity in cost of equipment, piping and civil engineering from country to country it is impossible to suggest even budget prices for installation of recycling systems. At minimum a crude basic non-automatic system such as shown at Fig. IV earlier could be installed for less than US \$ 1,000 for a 1 - 2 drum unit. Virtually only a pump, piping and collection pit are essential, whereas a more sophisticated unit for the same purpose could cost upwards of US \$ 10,000. (See Annex IV - Flant and Equipment Available for Tannery Effluent Treatment Projects).

However, provided that the level of sophistication of such recycling system is concommitant with the tanneries available human resources it may be firmly stated that the rewards of recycling are rapidly obtained. It is reported⁽⁶⁶⁾ "According to the size of the Tannery, the payback time of recycling equipment can be between $1\frac{1}{2} - 2\frac{1}{2}$ years for lime recycling and $\frac{1}{2} - 1$ year for chrome tanning floats".

CHAPTER IV

TREATMENT OF TANNERY EFFLUENT

INTRODUCTION

1 BACKGROUND

From the foregoing chapters it may be appreciated that the pollutants present in tannery effluent may be appreciably reduced by implementing more environmentally sound technologies. It is felt that in most situations a reasonable environmental standard may be achieved by coupling such "hetter environmental processing" with the removal of specific, possibly toxic, materials, e.g. sulphides and chromium. The residual effluent from such pretreatment will then only be significantly characterised by a high B.O.D. load.

In many circumstances, the dilution afforded by the recipient, may be able to cope with such partially treated load without undue ecological disturbance. In situations where the recipient does not afford sufficient dilution it is suggested that simple, relatively low capital cost processes, employing physico-chemical sedimentation techniques may prove satisfactory by removing 85 - 95% of suspended solids together with 45 - 70% of the B.O.D. Where local circumstances dictate that further treatment is essential a biological treatment is outlined employing an oxidation ditch, possibly the simplest and most robust secondary treatment system, proven in tannery effluent treatment.

The consultant is mindful of the need to allow low-cost implementation of tannery effluent treatment plants and attempts to give the basic system parameters only and assumes that actual implementation will involve maximum local construction, employing most suitable available low-cost domestic materials. A minimum of "imported technology" and plant only is recommended, and for such imported items, as are felt necessary, a possible 1982 guide price is quoted in this chapter. However at Annex IV a more detailed review of Flant and Equipment available with budget prices of 1984 may be found.

2 STRATEGY

This Paper accepts the philosophy that in most Developing Countries it is more realistic to install an easily run reliable treatment plant to remove up to 75% of pollutants at moderate cost, rather than attempt to

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remove over 95% of all pollutants at possibly ten-fold capital cost, in a sophisticated plant, beyond the technological expertise available, with a distinct possibility that within a few months such tender plant will be inoperative.

3. LOCATIONAL ASPECTS

The system to be installed at any particular tannery will be governed by the size of tannery, its throughput and volume and characteristics of effluent, the tannery's position viz-a-viz major areas of domestic habitation and the flow and condition of the recipient waters. No definitive parameters are available to guide such selection as actual choice of system to be implemented may only be made after an "on site" analysis of local circumstances. This Paper may, however, provide pointers to aid such selection, by local personnel, and will briefly review certain pertinent areas of interest.

N.B This Paper is specifically directed towards the needs of Least Developed Countries and in such circumstances it is assumed that tannery effluents will be discharged to surface waters (rivers or lakes) as P.O.T.Ws do not exist, except possibly in the centre of major or capital cities.

In the discussion in this chapter it will be assumed that the tannery is producing a mixed effluent (chrome tanning) with characteristics similar to those shown at Annex I, with a utilization of circa 45 litres/kg water, yielding suspended solids of 3,300 mg/litre and a $B.0.D._5$ of 1,300 mg/litre. Where effluents are known to have different basic characteristics the necessary adjustments will need to be made.

a) Recipient

As shown in Chapter II, calculations have shown that "to meet the water quality standard to support normal fish life a receiving stream should have at least a flow of 6 m^3/day stream flow per kg of hide processed/day".⁽¹⁾

Assuming utilization in the tannery of 45 litres/kg hide it may be suggested that $6 m^3$ (6,000 litres)/day stream flow can support 45 litres tannery effluent/day (i.e. a dilution of 133 fold) without undue ecological disturbance. A discharging tannery may feel it is not causing local problems if the recipient has an effective dilution <u>(all year round)</u> over 133 fold, without other significant local effluent discharges, and could enhance its position by taking positive steps to remove the major two materials which have some potential toxicity (sulphide and chrome).

If the dilution afforded by the recipient is less than 133 fold, or if others are also discharging industrial effluents locally, the effluent will need treating to proportionally lower the concentration of pollutant.

b) Joint Treatment Systems

The economies of scale for effluent treatment plants are quite large and if there are several tanneries within the locality it may be cost-effective to install a joint treatment plant. The possibility of having a joint tannery:municipal treatment plant could also be investigated in some locations. Economies of scale have been reported⁽¹⁾ suggesting, in the U.S.A., a six-fold reduction in capital cost, per unit, for a twenty-fold increase in tannery throughput. Data for India⁽¹⁾ showed almost a halving of unit cost with a ten-fold increase in throughput.

c) Locale

The question of the tannery's location in possibly densely populated urban areas or sparsely populated rural areas may influence the choice of technology of effluent treatment. In rural areas space may exist for lagoons and other operations, whereas in urban areas space may be limited. Possibly of equal significance in urban areas is the question of noise - some treatment systems operating 24 hours a day may produce significant noise levels (aerators etc.). However such noise may be limited by choice of alternate technology, i.e. immersed aerators which are quieter may replace floating aerators, and in any case, must be balanced against any improvement in general environment, if the noxious odours, associated with some tanneries, are removed.

B PRIMARY TREATMENT TECHNOLOGIES

To implement even basic effluent treatment technologies it appears essential to have, at some stage, the tannery liquors segregated into three streams :-

Lime Liquors (specifically sulphide bearing liquors, including water from fleshing and first delime wash). Chrome Liquors (including liquors from piling and sammying).

Other Liquors

Screening

Prior to discussion of treatment systems it must be noted that it is essential to ensure that all effluent streams are screened in some form to remove the large fragments which will otherwise block pipes, pumps and gullies.

A series of locally produced screens may prove efficient. These could be a series of two or three, ranging from a bar grid with apertures of 5 cms. down to a fine mesh of 0.5 cms. Such cheap locally produced screens would require regular cleaning (possibly a man permanently on duty).

A variety of "self cleaning" screens of patent wedge wire construction, are now available (Bauer Hydrasieve type). When correctly supplied such units are most economic and efficient, but it must be noted that many such units installed, possibly due to wrong specification, still need regular manual cleaning.

(Possible cost - 1 m^2 screen surface, (spacing 1 mm) = 6 - 18 m^3 /hour flow at circa U.S.\$ 3,000).

In practice, more efficient, maintenance free, operation appears to be obtained from the "brushed screens" (Parkwood type). Although such units may require greater floor area, and a power supply for the motor.

(Possible cost 1.2 x 1.0 m. - 1.6 mm perforations. 30 m³/hr flow. At circa U.S.\$ 3,500).

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Pumps

Although employing gravity where possible, in the majority of effluent treatment plants, the liquid must be pumped at least once during treatment. There are a wide variety of suitable pumps, but it must be noted that, even following screening, there may be a significant volume of small fragments, and it is essential that pumps are designed to handle such material on a continuous basis.

1. LIME/SULPHIDE LIQUORS

Although the sulphide content of tannery effluents, if well diluted, has only marginal effect on recipient water, there is little doubt that, given the malodorous nature and potential toxicity of H_2S gas, all efforts should be expended to separate sulphide bearing liquors and treat them to greatly lower the concentration of sulphides.

a) Catalytic Oxidation of Sulphides

The techniques for catalytic oxidation are now well established. Bailey and Humphreys in 1967 published a Paper⁽⁵⁴⁾ outlining a simple, low cost, technology to remove sulphides by aeration in the presence of a manganous catalyst. The process, a batch system, has been widely refined and proven in a multitude of tanneries. It is normal to carry out the process daily to avoid odours from storing old liquors.

The original proposal by the B.L.M.R.A. workers utilized tall towers (up to 5 or 6 m high) with the necessary air being introduced at the base. The diffused air was supplied from a relatively cheap, Rotary Vane Air Blower working via a network of standard activated sludge, Sintered Alundun dome diffusers. B.L.M.R.A. work suggested that the aeration intensity should be of the order of $0.3 \text{ m}^3/\text{minute per m}^2$ of tank cross section. Employing a catalyst concentration (manganous sulphate) of 100 mg/litre Mn⁺⁺, aeration for 4 - 6 hours, reduced the sulphide level from 2,000 mg/ litre down to 20 mg/litre S⁻.

It was originally suggested that as the catalyst was soluble it could be introduced undissolved to the system. However, more recently others suggested greater efficiency could be obtained if

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the catalyst was previously dissolved in water⁽⁵⁵⁾. Reports have been published⁽⁵⁶⁾ showing use of lower levels of catalyst, T.N.O. apparently obtained good results with L4 mg/litre Mn⁺⁺.

With a grid of diffusers at 30 cm centres the B.L.M.R.A. original work suggested each diffuser would need some 2.0 m³/hour air. A major advantage of a blower:diffuser

system is that costs (capital and running) are low and the small bubble aeration has a relatively high oxygen transfer efficiency (12 - 20%).

(Possible cost of an air blower to supply up to 200 m³/hour is $\langle U.S.$ \$ 1,000 and dome or candle diffusers only some

U.S.\$ 20 each).

Although in some employment the quartz (silica) diffusers are described as "self cleaning", this is not so given the high suspended solids of a used lime liquor, and if the diffusers are left inoperative in a lime liquor they will need regular cleaning to overcome clogging. If air is being blown in at all times when liquor is present this problem may be avoided.

It may also be possible to pass the liquor through a sedimentator prior to the catalytic oxidation - this would lower the suspended solids in the liquor being treated, to ease problems of clogging of diffusers, but the suspended solids in the sludge so extracted would still be sulphide contaminated, and prove more difficult to dispose of.

During the catalytic oxidation process some foaming may occur. (Mobilpar W was found in the initial B.L.M.R.A. trials to be a suitable anti-foaming agent. Practical operators have suggested the employment of a limited application of kerosine). More recently catalytic oxidation has been carried out employing surface aerators or robust submersible aerators. The choice of aerator will depend on local circumstances.

Surface turbine type aerators, being very robust, but quite noisy, are simple to install - usually float mounted and anchored to three lugs on the vessel's periphery. These are not subject to clogging and are certainly most suitable for large volume catalytic oxidation systems ($>100 \text{ m}^3$), are said to have oxygen transfer rates of circa 1 - 2 kg oxygen per kw/hour.

(Possible cost 1 h.p., smallest available, = circa U.S.\$ 6,000. 7.5 h.p. circa U.S.\$ 15,000).

Immersed aerators, with aspirating tubes, are appreciably quieter than surface aerators and may be employed within a tannery where perhaps an existent pit is converted to be a catalytic oxidation vessel. Oxygen transfer is reported at $\sum 2 \text{ kg}$ oxygen/kw/hour.

(Possible cost 2.5 kw (smallest model) circa U.S.\$ 3,500. 20 kw circa U.S.\$ 12,000).



NOTE :

Process vessels may be rectangular or round, constructed of suitable locally available materials. In some circumstances, in circular vessels, vertical baffles

may give improved performance overcoming the problem of the whole mass of liquor swirling in the vessel. Volume of vessels is governed by collectable sulphide-bearing floats, employed allowing some 20 - 30% freeboard to contain any foaming.

The size of aeration system may be calculated crudely, even if no analysis is available. Thus, knowing initial offer of sulphide could assume 50% available for catalytic oxidation. "1 gm sulphide (S[®]) corresponds to 3.94 gm technical Na₂S (62% pure)"⁽¹¹⁾.
Calculate sulphide content. To oxidize 1 kg of sulphide needs 0.75 kg oxygen^(From 11). Thus, (see earlier) can calculate kw installed requirement. Assume batch process of 4 - 6 hours convenient.

Alternatively, may calculate air volume required from blowers. 1 m³ air = 0.28 kg oxygen. If transfer efficiency is 12% 1 m³ air = 0.034 kg oxygen ie 30 m³ air = 1 kg oxygen.

The catalytic aeration system of oxidation as outlined above suffers from one major disadvantage. The oxidation does not proceed fully to the sulphate form. It is reported to oxidise to the thiosulphate form which then decomposes into a balance of sulphur and sulphite. If the liquor so treated is allowed to stand for some time sulphide is again formed and H_2S could be generated.

A recent presentation on this subject⁽⁵⁷⁾ outlined practical Stevens, treating all sulphide bearing experiences in this area. liquors (i.e. up to pickle) found that with the large volumes being handled a catalyst level of 50 - 75 mg/litre manganous sulphate reduced sulphide content from 800 ppm down to 5 ppm given $3\frac{1}{2}$ - 4 hours An air supply of 400 cubic feet of air/minute (680 $m^3/$ aeration. hour) was satisfactory for the 90 m^3 , initially with 800 mg/litre S^{$\frac{1}{5}$}. He reported pH 10.2 as being optimum pH for the treatment and suggested that at such pH level no reversion to sulphide was encountered. When however the pH of the aerated liquor was reduced to pH 8.5 - 9.0, to satisfy discharge requirements, reversion to sulphide occurred. Other reports (58) have suggested.... "that reconversion to sulphide only occurred when the aeration time was less than 16 hours."

Thus such simple catalytic oxidation is suitable for use when the effluent will be discharged rapidly or passed to a further stage of process where free oxygen is available. Such catalytic oxidation may not be suitable pretreatment for liquors which will be passed to anaerobic lagoons etc.

b) Other Sulphide Eradication Systems

(i) Chemical Oxidation

The treatment of sulphide bearing liquors by simple chemical oxidation techniques has been attempted employing

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hydrogen peroxide and potassium permanganate and other materials. However given the higher cost of chemicals and the need to pay foreign currency for these materials, they cannot be realistically employed in Developing Countries.

(ii) Precipitation Techniques

Ferrous sulphate and ferric chloride can be utilized to remove sulphides from solution by precipitation. The removal of sulphides by such a system is relatively simple and as well as removing sulphides such treatment also lowers the pH, due to precipitation of hydroxides, which causes partial precipitation of some protein matters present. Where such addition of iron salts is practised it is usually in the equalized mixed tannery effluent (see later this chapter:-Physico-Chemical Systems). Disadvantages of employing iron salts are :-

- :- that the coagulated material is dark in colour and if not effectively sedimented yields poor colour to final effluent,
- :- the sludge from this system is not dense, therefore its volume may be excessive.

2. REMOVAL OF CHROMIUM

As discussed in Chapter III D the precipitation of chrome is relatively simple and efficient. The efficiency of the total operation will be dependent on the ability to collect the major chrome The need for bearing liquors into the central chrome treatment unit. specific chrome flow treatment is governed by discharge conditions If no individual chrome flow treatment is undertaken relating to sludge. the chrome will be precipitated in the sludge formed at the equalizing tank - thus all sludge produced will be tainted with chrome. If there is need for the major sludge to be chrome-free this chrome flow treatment will isolate such chrome in a small sludge/slurry (which may be given special controlled dumping - but preferably being reused), leaving the general sludge virtually chrome-free.

To obtain an almost chrome-free supernatant it is suggested (50) that

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if the retan and other chrome bearing liquors have their pH raised to >8 (additions of lime) additions of aluminium salts (200 ppm Al³) and anionic polyelectrolytes (to 5 ppm) will give a good fast settling flocculant which may be settled out in a sedimentation vessel, yielding a clarified liquor of low chromium content. When settlement is complete the supernatant liquor containing circa 4 mg/litre Cr_2O_3 may be pumped forward to join the other streams of effluent. Magnesium



oxide could be employed as an alternate precipitating agent - See Chapter III.

Fig. XII gives an outline of the basic requirement. It is possible to employ only one pump, the suction pipe level and discharge pipes being

adjusted according to whether sludge, dissolved chrome or supernatant is being discharged. No sophisticated equipment or vessel is necessary. An old unutilized pit could be employed <u>UNLESS</u> the chrome precipitate is to be dissolved, in which case the vessel must be able to withstand the heat generated during resolublilization. Whether the valuable chrome precipitate is redissolved for reuse or pumped to a special sludge bed for drying, prior to controlled dumping, the major consideration is that the effluent is virtually chrome-free.

3. COMBINED EFFLUENT STREAM

a) Mix and Flow Balance - Equalization

Tannery effluent is normally generated spasmodically during an 8 - 12 hour period. For later treatment it is preferable to have a steady flow over 10 or 24 hours of uniform characteristics. Such steady flow avoids the need for specialized treatment plants to be overdimensioned to cater for peak flows.

Thus following individual flow treatment (sulphide and chrome) and screening, it is usual to mix and equalize all effluents in a balance tank. Such tank should preferably have a capacity of one day's effluent. From such equalization tank the effluent is pumped forward at a regular rate over the desired working period (i.e. if total daily effluent = 400 m^3 . One may pump at 17 m³/hour for 24 hours or 40 m³ for 10 hours). (If pumps available for this forward flow are too large their effective throughput may be adjusted, quite accurately, by inserting into the discharge line a T joint, with one controllable flow being directed back to the equalizing tank).

The level in the equalizing tank must not be allowed to fall below 30% of total volume to ensure there is always sufficient liquor available to allow equalization of inflowing effluents. This is best controlled using sturdy plastic cased mercury switches. (Possible cost two level regulators with control unit circa U.S.\$ 200)

Equalization promotes some neutralization and mutual precipitation. Thus given unhairing liquors of pH11.0 and pickle/ tan liquors $\langle pH 4.0$ the equalized liquor may have a pH of circa 9.0.

Any chrome present will be precipitated by the alkaline liquors from which some of the protein may also be coagulated. During the equalization it is necessary for the differing liquors to be well mixed to ensure uniformity and to maximise mutual precipitation and coagulation and it is essential that the suspended solids are not allowed to settle, and aerobic conditions maintained. To keep the materials from settling it is necessary to mechanically stir or inject air via some form of diffuser.

French workers (11) suggest an input of 40 watts per m³ is necessary to avoid settlement at this stage. Large mechanical rotors (1.5 - 3.5 m diameter) with slow rotation (50 - 100 r.p.m.)avoid a shear effect which could spoil later flocculation. Employing such stirrers the tank should have a width - depth ratio of circa 2 (with circular tanks, baffles may be necessary to ensure correct flow character).

A source of air injuition into the lower levels of an equalization tank can prove even more effective as, in addition to

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avoiding settlement of suspended solids, flocculation may be encouraged and anaerobic conditions avoided. Given a tank $2 - 4 \pm 1000$ m deep, an optimal air flow of $3 - 4 \pm 1000$ m² tank is reported⁽¹¹⁾.

Surface aerators are also suitable for use in equalising tanks.

4. PHYSICO - CHEMICAL TREATMENT.

Relatively simple technology allows the removal of up to 95% of suspended solids and possibly 70% of B.O.D. employing physico-chemical treatment.

Given efficient clarification (removal of suspended solids) the final effluent from such treatment should have minimal turbidity and colour and being virtually sulphide and chrome-free (as outlined earlier), should be acceptable for discharge in most circumstances in Developing Countries. Such treatment is low in capital requirement and the technology should be comprehensible and well within a tannery technologists' field of competence.

Only in rare circumstances should it be necessary in L.D.Cs to proceed to the higher capital intensive and difficult to control secondary stages of effluent treatment (biological) to remove the light levels of pollution remaining.

In essence the physico-chemical process outlined below is :condition i.e. pretreat the effluent by adding coagulants and flocculants in order to aid the sedimentation of suspended solids. This is followed by clarification - passing through a sedimentation tank which separates the suspended solids sludge from the supernatant, which is a clear liquor almost free of suspended solids and with much reduced B.O.D. levels.

a) Pretreatment

The C.T.C. publication "Pollution and Tanning"⁽¹¹⁾ defines :-

"Coagulation essentially consists in introducing into the water a product capable of uncharging the generally electronegative colloids present, hence forming a precipitate.

Flocculation is the agglomeration of uncharged colloids resulting from a series of successive collisions caused by a mechanical stirring process. A flocculant is thus above all a coagulation stimulant which increases the formation speed, cohesion and density of the floc, and consequently lessens its volume."

The materials most commonly employed are :-

(i) Coagulant

Alum (Aluminium Sulphate (- AL₂ $(SO_{l_1})_3$, 18 H₂0) Ferrous Sulphate (Fe SO_{l_1} , 7H₂0)

The dosages will depend on local circumstances and optimum conditions, dosages are usually found by on site experimentation, and may be governed by the effluent characteristics, equipment available, clarification level expected and flocculant (if employed). The most usual material employed is Alum. The C.T.C. workers suggest (11) a general usage of 200 mg/litre (0.2 kg per m³ effluent) Alum, but also quote increased efficiency at 400 mg/litre, whereas Giles (59) quotes roughly 800 mg/litre.

Ferrous Sulphate, employed at 500 mg/litre has several advantages i.e. is cheap and will effectively precipitate sulphides present, but has the disadvantage of bringing heavy colouration to both liquor and sludge, due to the formation of the black sulphide precipitate. In some systems both the above materials are employed. Poole $^{(62)}$ recently published data on the efficiency of a wide variety of coagulants including ferric sulphate and chloride, hexametaphosphate and magnesium carbonate, suggesting such materials could efficiently coagulate suspended solids. But given low cost of Alum, it is the most common coagulant employed.

(ii) Flocculants

Flocculants are usually long chain anionic polyelectrolytes, and are employed at levels of 1 - 10 mg/litre.

N.B. The polyelectrolytes are somewhat fragile - they are extremely viscous and stock solutions must be prepared carefully (as per manufacturers instructions) employing a slow speed mechanical stirrer.

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(iii) Dosing

Dosing of the necessary additions is critical and usually carried out employing a dosing pump. The chemical additions are prepared in standard solutions and the dosing pumps adjusted to inject the necessary volume per hour (cf the need for known effluent flow rate). Alternatively, on larger installations a flow meter may monitor effluent flow and be coupled to a dosing pump.

(For most installations the dosing pump should prove adequate. Possible cost of a single head pump - controllable doeing 0 - 50 litres/hour = circa U.S.\$ 1,000. A triple head pump (three independently adjustable flows, each 0 - 50 litre/hour) = circa U.S.\$ 2,500).

The additions are made separately to the equalized effluent. Efficient operation is reported (11) when the coagulant is added ... "in a vat where the water stops a short time (less than two minutes)" whereas ... "the flocculant will be added in a second vat where the volume is detained for a longer time (over ten minutes)." However, much depends on the system employed for the clarification, as in most cases the central core entry of the sedimentator will aid the flocculation and consequently dosing is sometimes carried out at the point of entry to the sedimentation vessel. See Fig. XVI for schematic layout.

Employing the dosing pumps it is possible to inject the chemical additions directly into the flow feed line and avoid the use of separate mixing vats.

(iv) pH

The optimum pH for alum precipitation of lime is said⁽⁵⁹⁾ to be pH 7 - 10. Practical operators have generally found the natural pH of the mixed liquors to be within this range. If, due to recycling or other measures such equalized liquor is not within this range, additions of acid/alkali may be necessitated. pH adjustment, if necessary, is best carried out employing a pH control unit incorporating a pH monitor, coupled to two dosing pumps.

(Possible budget price - pH monitor and two dosing pumps = U.S.\$ 4,000).

b) Sedimentation

There are two possible types of sedimentation vessels.

(i) <u>Horizontal Flow Tanks</u> - the most basic unit may not be seriously considered if high levels of efficiency are required. An outline is given at Fig. XIII of such a basic unit, but unless they are mechanically scraped (expensive, not usually possible in a low cost, locally produced, version), they soon become clogged and may be operated ineffectually with the tank full of sludge and the effluent passing over the surface without complete sedimentation occurring.



Horizontal Flow Sedimentation Tanks should be dimensioned so as to have a six hour retention time. As such units require regular desludging it is necessary to have a spare tank. Desludging may be effected by gravity or sludge pump after the supernatant has been pumped or syphoned to the standby unit.

For large flows - over 1000 m^3 /day the mechanically scraped units may be cost effective.

(ii) <u>Vertical Sedimentation Tanks</u> - of cylindrical local fabrication seem the most efficient and cost effective primary sedimentators for tanneries, see Fig. XIV. They may be fabricated of steel (with epoxy coating), stainless steel, fibreglass or constructed in rectangular form employing concrete or wood, as available.

Given the 60° angles the walls are self-desludging. The basic requirements are for some degree of turbulence at the inlet to ensure mixing and encouraging flocculation. Turbulence



must be avoided in the rest of the unit. Employing gravity, the solids settle and concentrate at the base, from where they may be drawn off via the valve. The clarified effluent is gently drawn off at the top. The upward flow rate should be in the range $1 \cdot 0 - 1 \cdot 5 \text{ m}^3/\text{m}^2/\text{hour.}$

(iii) <u>Flotation</u> - An alternative method of removing suspended solids is by "flotation" out of the mixed effluent. Two major techniques have been employed in general waste water treatment and recently trials on tannery effluent have been attempted.

:- Electroflotation

The effluent is subjected to electrolysis forming gas bubbles (hyrogen and oxygen) which lift suspended matters to the surface from whence they may be removed.

:- Air Flotation

Air is dissolved in the recycled effluent under pressure when this pressure is subsequently lowered in the treatment vessel small air bubbles are released carrying the suspended solids to the surface.

B.L.M.R.A. workers published $^{(60)}$ details of flotation experiments on tannery effluent, recording positive results. They calculated that in 1978 a dissolved air flotation plant to process 200 m³/day of mixed beamhouse liquors would cost £ Stg. £37,500. (Circa U.S.\$ 72,500).

Air and foam flotation units are included in some "package" effluent treatment units, said to cost from U.S.\$ 40,000 upwards.

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The advantages of air flotation are the compactness of the treatment unit, coupled with sludges of high solids content $(15\%)^{(60)}$ however, this is offset by high chemical costs to obtain optimum pH. The B.L.M.R.A. workers⁽⁶⁰⁾ suggested optimum conditions with dissolved air flotation was pH 4.0 with dosage of 500 mg/l aluminium sulphate 5 mg/l anionic polyelectrolyte (Nalfloc 676). However other workers have carried out flotation at high pH levels.

The consultant believes that "Flotation" will, in future be a significant system for tannery effluent treatment, but today, given the high chemical requirement (acid to reach pH μ ·O) and the relatively early ϵ age of development of the systems, such plant may not yet be suitable for Developing Countries (except the N.I.Cs).

c) Efficiency of Sedimentation

C.T.C. report⁽¹¹⁾ that additions of 400 mg/litre alum added to equalized tannery effluent allowed the following reductions :-

70% B.O.D₅ load reduction

80% C.O.D. load reduction

97.5% Suspended Solids reduction

Poole (62) reports on the efficiency of various chemicals employed to aid sedimentation of tannery effluents as may be seen at Table IX.

TABLE IN EFFECT OF VARIOUS CHEMICALS ON TOTAL SUSPENDED				
<u>s</u> c	LIDS AND B.O.D. IN A COMP	OSITE EFFLUENT SAMPLE.		
Chemical Dosage	Total Suspended Solids Reduction	B.O.D. Reduction		
Alum - 500 mg/l	86	43		
Alum + Polymer	87	53		
Ferric Chloride 2	0 mg/l 76	22		

Giles⁽⁵⁹⁾ employing alum, as primary coagulant, at up to 800 mg/litre, plus 10 mg/litre of an anionic polyelectrolyte, reports on clarification efficiences; showing reduction of suspended solids by 99% and B.O.D.₅ by 90%.

d) <u>Possible Effluent Characteristics After Physico-Chemical</u> Treatment

If tannery effluent is treated as outlined in Fig. XVI i.e. Catalytic oxidation of unhairing liquors - precipitation of chrome equalization - followed by flocculation and coagulation, prior to an efficient clarification, one could expect nearly $S^{=}$ and Cr^{+++} free effluent with basic characteristics as shown in Table X.

TABLE X	FINAL EFFLUENT CHARACTERISTICS					
	Original Effluent	Efficient Clarification	Mediocre Clarification			
Suspended Solids	3,300 mg/l	(Reduction) (95%) 165 mg/1	(Reduction) (85%) 495 mg/1			
B.O.D.5	1,300 mg/l	(70%) 390 mg/1	(45%) 715 mg/l			

AT THESE LEVELS THE EFFLUENTS FREE OF S⁼ AND Cr⁺⁺⁺ SHOULD BE ACCEPTABLE FOR DISCHARGE INTO SURFACE WATERS IN MOST SITUATIONS IN DEVELOPING COUNTRIES.

e) Sludge Handling/Disposal

The sludge slurry obtained from the sedimentation system outlined earlier should be free of sulphides and chrome and, as such, with its high lime content in many areas it will prove acceptable as an agricultural fertilizer/conditioner. Certainly it must be processed rapidly to avoid reversion to sulphides.

Sludge at the 3 - 5% solids often yielded by primary sedimentation is only effectively handled by pumping or gravity. Given available land for controlled dumping, tanker transport may be the simplest system of disposal.

(i)Drying Beds - may be recommended for smallmedium tanneries, not in prime urban locations as the land requirement may be great (see below). Sludge drying beds require low capital, but are labour intensive as theymmust usually be manually emptied when the material is dried. Sludge may be shovelled when solids content is circa 25/30% at which point the cake may be removed for dumping or agricultural use. Smell is reported from some sludge beds and is said to be minimised by sprinkling the surface with hydrated lime.

The layer of sand, usually removed together with the sludge cake, must be replaced.

Volume of Sludge

The volume of sludge may be calculated from basic project Thus, assuming a daily flow of 100 m^3 with an parameters. "efficient clarification" as at Table X :-

Suspended Solids

Suspended Sofias	Drv Solids
400 m ³ at 3,300 mg/l = 1,320 kgs/day @ 95% removal	1,250 kg/day
B.C.D. (assume 50% of B.O.D. removed is attributable	

to Suspended Solids) a crude calculation may be made:-400 m³ at 1,300 mg/l = 520 kg/day @ 50% of 45% removed _ 117 kg/day

Total Sludge approximately 1,400 kg/day

If the sludge is in a 4% solids slurry it will occupy approximately 35 m³ daily (a rule of thumb suggests sludge volume = 8 - 12% of effluent volume if employing 30/50 litre/kg water.

Construction of Drying Beds

Sludge drying beds are normally constructed employing layers of filtering media with agricultural drainage pipes at the base to collect liquid effluent which should be recycled back to the equalization tank, for further processing. Fig. XV shows typical sludge drying bed sectional detail.

Area of Drying Beds

The daily production of 35 m³ sludge slurry may be spread on drying beds to a depth of 0.5 m i.e would require 70 m² bed/day.

Convenient size 14 m x 5 m.



Drying period may vary from 2 - 4 weeks dependent on local conditions and the degree of chemical conditioning received. If 5 day working week would require 10 - 20 drying beds dimensioned as above. (Total area required 700 - 1,400 m²)

(ii) Alternative Sludge Dewatering Systems

:- <u>Thickeners.</u> Sludge thickeners, similar to the sedimentation tanks outlined earlier, can be employed to further thicken sludges to 10% solids in one day. However, even when so thickened they are still difficult to handle and require further treatment (i.e. drying beds or alternates below).

:- <u>Filter Presses</u>. As with most mechanical dewatering systems some conditioning of the slurry is necessary, lime, ferrous sulphate and polyelectrolyte are usually employed. Size of the filter press may be calculated from volume of expected sludge. Due to high capital and running costs filter presses are being phased out in favour of :-

:- <u>Continuous Belt Dewatering Machines</u>. The machines have recently been developed - as with filter presses the slurry needs conditioning and most units marketed have an integral dosing/ conditioning unit. The advantage of these machines is their relatively low capital cost, and they may be recommended for tanneries with effluent volumes of $\lambda 100 \text{ m}^3/\text{day}$. The continuous belt machines dewater down to 20 - 30% solids content - not as dry as filter presses but the material is easily handled. (Possible cost of continuous belt dewatering machine to process $50 \text{ m}^3/\text{day slurry}$ (2 - 3% solids) = circa U.S.\$ 30,000 - 50,000).

As yet, small belt dewatering machines are not available at reasonable capital level, however, there have been rapid development in this sector in the immediate past, and one may



hope that within a few years moderately priced small continuous belt dewatering machines may be available, at which time they could be recommended to small - medium sized tanneries in Developing Countries. (See Annex IV for typical costs/sizes of units available).

C SECONDARY TREATMENT

It is considered that in most locations in Developing Countries the physico-chemical treatment outlined earlier which, if well controlled, could yield a discharge standard of 200 mg/l S.S. and 400 mg/l B.O.D._c, should be acceptable to many local authorities.

In those few cases where a more purified effluent is essential recourse to biological treatment systems may be necessitated. There is a wide choice of biological treatment systems amongst which are :

> Biological Filters Activated Sludge (conventional) Activated Sludge (Oxidation Ditch) Lagooning (Aerated, Facultative and Anaerobic)

The consultant would agree that all the above systems have been proven in treatment of tannery effluent, but feels that the oxidation ditch system is suitably robust to withstand the occasional shock load and other irregularities (power losses, etc. leading to non-continuous production) which may be encountered at tanneries in Developing Countries. Whereas some of the other systems may be poisoned by such shock loads. Selection of secondary treatment system is governed by tannery location, land availability, technical expertise available, local equipment and energy costs. The following systems could be employed :-

1. OXIDATION DITCH

The principle of activated sludge treatment is that the "organically polluted effluent is brought into contact with a very large concentration of aerobic bacteria and other micro-organisms present in the form of a flocculant biological agglomerate known as "activated sludge" ".(1)

In the conventional activated sludge system, the sludge floc is kept in contact with the liquid phase employing surface aerators or diffused air systems, in rectangular tanks, which additionally supply the oxygen to maintain the necessary aerobic conditions. The organic material in the effluent is effectively removed by the biological activity.

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In order to maintain the necessary high level concentration of the microbiological floc in the process vessel, the effluent, after treatment, must pass through a sedimentation vessel (or other system) and the majority of the activated sludge floc returned to the process vessel.

Work at T.N.O. in Holland showed a low load activated sludge system employing an "oxidation ditch" could be suitable for tannery and/or domestic effluents. The Dutch work led to the installation of a number of Fasveer ditches in tanneries.

In essence the Pasveer ditch differs from the conventional activated sludge treatment in several ways :-

- (i) The treatment vessel is an annular tank employing rotating steel brush aerators to keep the sludge floc in suspension, ensure adequate hydraulic flow and supply the necessary air.
- (ii) The larger retention time and lower organic loading has shown itself to be more suitable to with tand the variable character and flow of effluent and shock loads experienced in the tanning industry.
- (iii) A further useful consequence of the lower rate of loading is the substantially reduced quantity of sludge produced, i.e. 0.3 kg of sludge solids/kg of B.O.D. removed, as compared with about 1.0 kg/kg of B.O.D. removed for a conventional activated sludge plant. ⁽¹⁾

The Pasveer ditch is relatively cheap with low maintenance, and when properly commissioned may yield effluents of satisfactory quality - down to 10 mg/litre⁽⁶³⁾.

Suppliers of the rotors, given basic project parameters are prepared to give free assistance with the design of a specific oxidation ditch.

Loading rates are reported (11) to be from 250 - 500 gms BOD₅/m³/day. Retention time of 2 - 4 days. A typical example may be calculated :-Thus 400 m³/day effluent, if given fair efficiency primary sedimentation could have a B.O.D.₅ of 500 mg/litre (0.5 kg/m³) = 200 kg B.O.D. At loading of 0.25 kg B.O.D.₅/m³/day would require 800 m³. 3 days retention would suggest 1,200 m³ ditch, which figure would give a safety margin.

Oxygen transfer by rotors varies according to the depth of immersion (adjusted by raising or lowering water level) and may be from :-

2 kg oxygen linear metre rotor (10 cm immersion) i.e. 48 kg/m/day 96 kg/m/day to 4 kg oxygen linear metre rotor (20 cm immersion) i.e.

Allowing safety margin, manufacturers usually suggest 1 m rotor = circa 30 kg B.O.D.,/day at 13 cm immersion, therefore the 200 kg B.O.D. would require 6.7 linear m of rotor - Possibly a minimum of 2 x 3.5 m. Installed capacity = 2 x 10 nr. Power Demand = 2 x μ θ HP = 0.9 Kw per Kg B.O.D. (Budget Price of 2 x 3.5 rotors (complete unit with motors and bridge), $(2 \times US \$ 12,000 = US \$ 24,000).$

Typical oxidation ditch layout may be seen at Fig. XVII. Opinion varies as to how much pretreatment should be given prior to processing It is generally agreed th bit is best practice in an oxidation ditch.

to remove sulphides and chromium to avoid any possible toxic effect to the biological mass.

Some screening and sedimentation is certainly essential, but whether it is necessary to chemically coagulate prior to sedimentation seems uncertain, as many authorities feel that the ditch itself is the most cost effective treatment process.

Practical operational outlines for oxidation ditches



may be gleaned from a recent Paper by Bailey and Plowright⁽⁶⁵⁾ which Berk⁽⁶⁴⁾ gives design data details a ditch installation in the U.K. and operational efficiency parameters for oxidation ditches operating on packing house and dairy wastes, which may have some relevance.

The materials of construction and dimensions of oxidation ditches are governed by the scale of the project. Ditches up to volume of 12 - 1300 m³ are operated by 70 or 80 cm rotors, normally constructed by excavation of shallow ditch of less than 2 m deep with sloping sides, which is then butyl as section :spray concreted. lined or

A ditch of 250 m³ volume may have total length 36 m. Total width 8 m Effective depth 1.8 m

A ditch of 1,300 m³ volume may have total length 63 m. Total width 15 m Effective depth 1.8 m

Larger units - over 1,200 m³ volume may have 1 m or even larger rotors in reinforced concreted structures, with vertical walls.

Oxidation ditches normally need small additions of a nutrient phosphorus - which is essential for the biological activity and is not available in sufficient strength in tannery effluents. Little seems to have been published on nutrient levels necessary, but one personal communication from an oxidation ditch operator suggested the addition of 10 kg day fertilizer $(18.5\% P_2 O_5)$, per 100 m³ effluent/day, as suitable.

The level of biological floc must be controlled by recycling the floc or discharging it as sludge according to condition. It is said that M.L.S.S. (Mixed Liquor Suspended Solids) should be between 3,500 and 5,000 mg/litre. But levels of 2,500 have been employed. Practical advice suggests that in the absence of analytical facilities a rule of thumb test may be applicable... "Fill a measuring cylinder with a sample of the agitated liquid - allow it to settle 30 minutes. After settling if approximately 20% of volume is seen as floc deposit - conditions are satisfactory".

It is possible to avoid the installation of a sedimentation tank by the following means :- Four times a day the rotor could be stopped for $\frac{1}{2}$ hour - the floc will settle - an adjustable weir could be operated to allow discharge of supernatant (1/4 day's effluent). The rotor may be restarted once the discharge has been effected and the weir readjusted.

The return of the floc from the sedimentation tank to the oxidation ditch is said to be best carried out employing a sludge return wheel. (Bucket type scoops on a wheel), as such wheel is said not to damage the floc. However in some installations pumps are employed without noticeable harm.

Commissioning of oxidation ditches is normally aided by acquirement of activated sludge for a local P.O.T.W. However in most Developing Countries such P.O.T.Ws do not exist and the floc must be built up slowly.

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Initially only limited volume of effluent being allowed to inter the ditch, until an increasing floc of activated sludge allows everincreasing volume to enter the ditch.

All reports suggest the. over 95% removal of $B.0.D._5$ is possible employing an oxidation ditch, i.e. a liquor with initial $B \ 0.D._5$ of 500 mg/litre could be expected to be discharged at <25 mg/litre at which level effluent is acceptable to all river authorities.

2. ACTIVATED SLUDGE

A wide choice of treatments may be effected employing activated sludge techniques (including oxidation ditches as outlined earlier). In practice, in addition to oxidation ditches, two alternate forms of treatment are often employed for secondary treatment of tannery effluents.

a) High Load Activated Jludge

This system occupies the smallest possible land area, as it is usually effected employing a rectangular vessel of some 3 m or more depth, with the necessary aeration and mixing obtained from surface or immersed aerators or diffused aeration devices Retention times of 6 -12 hours usually sufficing. (see Annex IV). Thus, for a situation as detailed earlier (at Oxidation Ditch), with 400 m³/day flow with a fair primary treatment yielding a secondary influent at circa 500 mg/l B.O.D.₅ (i.e. 200 Kg B.O.D./day) a tank of 133 m³ volume could suffice - possibly 8 m x 4 m x 4 m deep -2 aerators of 4 or 5 Kw could be employed (dependent on characteristics). Such unit would have an organic loading of 1.5 Kg B.O.D./m³ day and would require a high level of sludge return employing efficient sedimentation unit to ensure the MLSS was kept at circa 5000 mg/litre. It must be noted that although such a system is proven in tannery effluent treatment it is not resilient to shock loading and may prove unsuitable to the irregular conditions found in developing countries. (Energy input approaching 1.0 Kw per Kg B.O.D._{ζ}).

b) Extended Aeration/Low Load Activated Sludge

An adapted form of activated sludge employing longer retention

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time yields much greater protection against shock loading due to the system's enhanced dilution. Such systems however may require increased energy utilization. "Extended aeration" may be operated with retention times of 1 - 3 days with the level of MLSS kept between 1,500 and 2,500 mg/litre by means of recycling of the floc from the secondary sedimentation unit. Thus for the $\frac{1}{400}$ m³/d discussed previously the following parameters could be utilized :- $1\frac{1}{2}$ day retention = Vessel of 600 m³ eg 25 m x 8 x 3 m deep with necessary aeration supplied by 6 aerators of 1.5 or 2.0 Kw., (or other aeration device - see characteristics Annex IV). (Energy input >1.0 Kw per Kg B.O.D._c).

NOTE: With regard to selection of systems it is recently reported⁽⁶⁷⁾ "The investment costs of an oxidation ditch plant are about 20% less compared with the investments of a conventional activated sludge treatment. The exploitation costs are about 8% higher in 1982, mainly caused by difference in energy consumption".

3. LAGOONS

A wide variety of lagooning techniques have been recommended for treatment of tannery effluents (1) (11).

<u>Anaerobic Lagoons</u> have been reported (1) to remove up to 85% of B.O.D. in ten days, however they normally produce significant air pollution - may encourage reversion to sulphides with discharges of hydrogen sulphide and can only be recommended in remote locations. Cost of such lagoons is negligible as the only requirement is a depth of 3 m or so when anaerobic conditions will be rapidly established.

Facultative Lagoons which operate with three distinct layers :-

Surface	layer	. –	Aerobic
Central	layer	-	Facultative
Lower	layer	-	Anaerobic

Such lagoons/ponds may theoretically operate employing natural photo-synthesis however under such conditions it is subject to vagaries of climatic variation and may not be controlled, and thus is suitable in few locations only.

<u>Aerated Lagoons</u> have been operated in many tanneries with inputs of from 10 - 30 w/m³, usually employing surface aeration devices. Reported results of such treatment are somewhat inconsistent, and no firm recommendation may be given.

<u>Facultative Aerated Lagoons</u> have been pioneered in France⁽¹¹⁾ and it is reported that following an efficient primary treatment system B.O.D.₅ reduction from 660 mg/l to 90 mg/l is effected employing only 2 w/m₃ at 9 days retention. The system is said to receive sufficient oxygen to allow "biological purification activity" with insufficient stirring capacity to maintain suspension of solids both added and those produced by mineralization. A diagrammatic representation of such facultative aerated lagoon may be seen at <u>Fig. XVIII</u>, which is adapted from "Tannery and Pollution"⁽¹¹⁾ where the scheme is detailed. In summary for a 2,000 m³/day input two lagoons are employed :- No. i - 3,000 m³

No. 2 - $15,000 \text{ m}^3$ Total 18,000 m³ ie 9 days retention



The two Turbo-Oxiders are float mounted and facilitate the circular motion in Lagoon No. 1 which is 2.5 m deep. Lagoon No. 2 which is sub-divided into four compartments has 1.7 m useful depth and is fitted with aerators as shown. The system generates zones of complete and partial aeration in addition to anaerobic zones out of contact with

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the aerators where deposition of solids occurs and anerobic activity is encouraged. Prima facie the system is low in both installation and running costs, however, this assumes a large availability of land as the 2,000 m³ day require almost 10,000 m² area of lagoon. In areas where ground water contamination could occur the cost of lining such vessel would mitigate against the apparent low installation cost.

Of more fundamental importance is the need for draining and desludging the complete lagoons every 5 - 10 years, as such may occupy up to 3 months, it is possible that the system needs some modification. It may prove feasible to construct the lagoons so that there were 3 systems in parallel - two being operated at any one time and the third unit out of operation for desludging. Such expansion by 50% of the system would however increase the total capacity of the treatment unit to over 13 days retention, and require greater surface area (almost 7.5 m^2 lagoon per m³ effluent/day), but could be justified in areas of high energy cost.

Evaporation Lagoons. May be operated in remote arid areas, with dimensions governed by local, known, evaporation rates. However, in such arid areas it is usually considered anti-social to regularly evaporate significant quantities of water which, with minimal treatment, could be utilized for society's benefit. Additionally such evaporation lagoons may develop anaerobic characteristics with malodorous discharge.

NOTE: WARNING WITH REFERENCE TO FOLLUTION OF GROUND WATERS

During the installation and operation of tanks, basins and lagoons etc. due consideration must be given to local geological conditions. Where full geological data is not available as to the permeability of the subsoils it may be expedient to line all such units (Butyl sheet etc. or concrete) to avoid contamination of ground waters by leaching from the treatment plant.

					-	
		hrome annage		Vegetable Tannage	Rar	ige
Alkalinity	eq/t		750			
Total solids	kg/t		675		3 50 -	1,250
Total ash	kg/t		375		250 -	450
Suspended Solids	kg/t	150		75	70 -	200
Ash in suspended Solids	kg/t	60		25	25 -	60
Settled Solids (2 h)	m ³ /t	6		3	1.5 -	• 7•5
BOD ₅	kg/t	60		85	40 -	100
IOD	kg/t		10			
KMnO ₄ - value	kg 0 ₂ /t	70		120		
$COD (K_2 Cr_2 O_7)$	kg/t		175		120 -	280
Sulphide	kg/t		7			
Total Nitrogen	kg/t		10			
Ammonia Nitrogen	kg/t		3			
Chrome	kg/t	4.5		0		
Chloride	kg/t		160			
Sulphate	kg/t		40			
Phosphor	kg/t		0•07			

ANNEX IA

AMOUNTS OF POLLUTION PER TON OF RAW MATERIAL (SALT WEIGHT)

Source:

Ref⁽¹⁾ "Environmental Considerations in the Leather Producing Industry".

ANNEX I B

POSSIBLE COMPOSITION OF TYFICAL "NON-ENVIRONMENTALLY SOUND"

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TANNERY EFFLUENT

		Chrome Tanna	ge <u>Ve</u>	getable Tannage
рН			ca. 10	
Total Solids	mg/1		15,000	
Total Ash	mg/ 1	,	8,000	
Suspended Solids	mg/l	3,300		1,700
Ash in suspended solids	mg/1	1,300		600
BOD5	mg /1	1,300		1,900
KMnO ₄ - value	mg 0 ₂ /1	1,600		2,700
$COD (K_2 Cr_2 O_7)$	mg/l	3,500		4,500
Sulphide	mg/ 1		160	
Total Nitrogen	mg/ 1		220	
Ammonia Nitrogen	mg/l		65	
Chrome (Cr)	mg/l	100		-
Chloride (Cl ⁻)	mg/1		3,500	
Sulphate $(SO_{\underline{l}})$	mg/ 1		900	
Phosphor (P)	ng/ 1		2	
Ether Extractable	mg/ 1		400	

Source:

Calculated from Annex I A assuming, in general, water consumption of 45 1/kg.

ANNEX II

TYPICAL OUTLINE PROCESS - "SEMI-TRADITIONAL TECHNOLOGY"

AFRICAN DRY HIDES FOR CORRECTED GRAIN UPPER LEATHER

PROCESS		INPUTS/CONTROLS	DURATION
SOAK	Weigh	Calculate estimated soaked weight = basis	
(Rehydrate)		for lime process (soaked weight may be as	
		dry weight x 2.9)	
	Scak	In pit with changes of water -	2 days
		Water usage may be up to 300% on expected	
		soaked weight. (Number of changes of	
		water and duration of soaking dependent	
		on cure condition and ambient temperature).	
		Total Water Usage may exceed 1,000%	
	117	Bacteriacide may be necessitated.	
	Dry Drum & Wash	According to condition	3 hours
	Green Fle	sh On Machine (May need "siding" first)	
LIME in Drum		200% Water at 28°C	
		4.0% Lime (Hydrated)	
		0.5% Glucose	
		1.5% Sodium Sulphide	
		Drum	1 hour
	Add	2.0% Sodium Sulphide	
	Drum	At intervals for balance of	24 hours
	Haul		
	Flesh	On Machine	
	Round - T	rim - Weigh = Basis for Delime and Tan	
DELIME & TAN	Wash in D	rum Running Water for	15 minutes
	Drain	2	
	Dulime	70% Water at 25°C	
		2% Sodium Bisulphite	
	Drum	(Test Phenol Phthalein)	15 minutes

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TYPICAL OUTLINE PROCESS - "SEMI-TRADITIONAL TECHNOLOGY" (continued)

	Add Bate	0.3% Pancreatic Bate	
	Drum	(Test Pancreatic Bate)	Dependent on Substance
	<u>Drain</u>		
	Pickle	70% Water at 25°C	
		6% Salt	
		1.2% Sulphuric Acid	
	Drum		- ! hour
	Add	0.5% Formic Acid	
	Drum		$-\frac{1}{2}$ hour
	<u>Add</u>	12% Self Basifying Chrome	
	Drum		- 6 - 8 hours
		LAY OVERNIGHT	
	Haul		
	Pile		- 48 hours
	Samm	NOW IN "WET BLUE" STATE	
	C-14		
	Split		
	Snave	- hasta for later success	
	weign	- Dasis for later process	
RETAN/DIE	Wash in Drum	Twice 300% Water at 30°C	- 15 minutes
	Neutralize	100% Water at 35°C	
		1% Calcium Formate	
	Drum		- 30 minutes
	Add	0.25% Sod. Bicarbonate	
	Drum		- 15 minutes
	Wash	Twice 300% Water at 50°C	
		1 🖇 Dye	
	Drum		- 15 minutes
	Add	3% Syntan	
		1% Sulphited Oil	
	Drum		- 15 minutes
	<u>Add</u>	4% Minosa Extract	
	Drum		- 15 minutes
	Add	2% Resin	
	Drum		- 30 minutes







MICROCOPY RESOLUTION TEST CHART

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TYPICAL OUTLINE PROCESS - "SEMI-TRADITIONAL TECHNOLOGY" (continued)

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Fat Liquor	100% Water at 55°C	
	3% Light Sulphated Cod Oil	
	1% Raw Cod 011	
	2% Filler (Soya or other flour)	
Drum	- 45 minut	es
Add	0.5% Cationic Oil	
Drum	- 15 minut	æs
Rinse		
Haul		
Semm	On Machine	
Set	On Machine	
Paste Dry	On Glass Plates	
Hand Condition, Stake	/ On Machine	
Pole Dry		
Sort/Select		
	NOW IN A CRUST STATE	

FINISH TO REQUIREMENT: TYPICALLY:-

PROCESS

•

Plate	Hydraulic Press
Buff	By Machine
Dust	By Machine
Impregnate	By Spray or Pad
Plate	Hydraulic Press
Rebuff	By Machine
Dust	By Machine
Pad Pigment	Hand Pad or Machine
Spray Pigment	Hand or Auto Spray
Plate/Emboss	Hydraulic Press
Top	Hand or Auto Spray
Measure	By Machine
Grade/Select	By Hand

NOW FINISHED SHOE UPPER LEATHER

ANNEX III GLOSSARY

- B.O.D. <u>Biochemical Oxygen Demand</u> is a measure of quantity of oxygen which may be consumed while biologically degrading the organic constituents. The test is carried out over five days and the result expressed as B.O.D.₅.
- C.O.D. <u>Chemical Oxygen Demand</u> (C.O.D.) is a measure of the quantity of oxygen consumed chemically in order to oxidise the constituents of an effluent. This test may be carried out by two differing methods employing Potassium Permanganate yielding a P.V. value or Potassium Bichromate yielding a C.O.D. $(K_2Cr_2O_7)$ value
- * Full Chrome The adjective "full" is sometimes added to "chrome tanned" (tanned) to emphasize that the leather has not been tanned by the semi-chrome or combination chrome processes.
- * Grain a. The outer, or hair side, layer of a hide or skin that has been split into two or more layers.

b. The pattern visible on the outer surface of a hide or skin after the hair or wool has been removed.

- * Leather A general term for hide or skin which still retains its original fibrous structure more or less intact, and which has been treated so as to be imputrescible even after treatment with water.
- * Retaining The process of subjecting a skin, which has been first more or less completely tanned by one process or one kind or blend of tanning materials, to a second tanning process, involving similar or, more usually, different tanning materials.
- * Split The under layer of a hide or skin, or part of a hide or skin other than the outer layer, separated by splitting, or leather made therefrom.

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GLOSSARY (Continued)

Suspended Solids refers to the various suspended solids which are capable of being separated from the liquor by filtration.

Total Solids refers to both dissolved and suspended solids in the effluent.

Turbidity a measure of the light-transmitting properties of water is another test used to indicate the quality of waste discharges and natural waters with respect to colloidal matter. Colloidal matter will scatter or absorb light and thus prevent its transmission.

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

> From British Standard 2780: 1956 - British Standards Institution From "Wastewater Engineering" Published by Metcalf & Eddy Inc.

From "Leather Technical Dictionary" Eduard Roether Verlag Darmstadt.

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ANNEX IV

PLANT AND EQUIPMENT AVAILABLE FOR TANNERY

EFFLUENT TREATMENT PROJECTS

I INTRODUCTION

A SCOPE AND LIMITATIONS

The summarized terms of reference relating to the preparation of this Annex were to prepare "a comprehensive Technical Annex of some $\frac{10}{50}$ pages which should detail and analyse the plant and equipment currently available for utilization within tannery effluent treatment schemes".

In pursuance of this objective, contact was made with over 150 companies thought to be active in the manufacture and supply of suitable equipment. As a result of follow-up activity, detailed data was obtained from over 100 companies which forms the basis for this Annex. (Responses received after 31.1.84 are not able to be included).

The suppliers with whom contact was made were either of international repute in the field, or selected from national directories. At an early stage in the selection of suppliers it became obvious that the list of suppliers and their products could not be considered exhaustive, as from directories alone several thousand potential suppliers could be listed. Accordingly it was felt expedient to attempt general coverage only within six countries : Brazil, Denmark, Italy, F.R.G., U.K., U.S.A. Possibly at a later date UNIDO may attempt to broaden the data base by expanding this preliminary assignment.

Of necessity, a Paper of this brevity must be directed towards major items of equipment only, thus small but essential items and possibly costly items such as pipes, valves, electric controls etc. which are not of a specialised nature are not reviewed here. Some items of equipment are produced in a multiplicity of sizes and styles; therefore to limit the data it was, in some areas, felt expedient to seek details and quotations relating to equipment suitable for tanneries at three different scales :-

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		EFFLUENT
Small Tannery	- 50 hides/day - Raw to Finished =	50 m ³ /day
Medium Tannery	- 300 hides/day - Raw to Finished =	300 m ³ /day
Large Tannery	-1,000 hiles/day - Raw to Finished =	1,000 m ³ /day

A major objective of this Annex is to make available basic sectoral data to those in developing countries who may wish to prepare their own projects and who have only limited local supply of such specialised equipment. To this end this Annex only covers suppliers who are willing to handle individual units. Suppliers who are only prepared to install complete projects are thus excluded.

B SPECIFICATION AND PRICES QUOTED

Indicative Budget Frices were sought, on an "ex factory" or "F.O.B basis", and it must be appreciated that such "Budget Prices" may be subject to - 20% according to the real situation and accessories required.

Budget Frices, where necessary, were converted to a US \$ basis at January 1984, employing the following conversion rates :

Brazil	1,000.00	Cruzeiro	=	US \$ 1.00
Denmark	9.92	Kroner	=	US \$ 1.00
Italy	1,662	Lira	=	US \$ 1.00
F.R.G.	2.69	DM	=	Π S \$ 1 -00
U.K.	£ Sterlin	g 0-71	=	US \$ 1.00

It may also be pertinent to note that the apparent wide margins between cost of equipment of nominally similar specification may reflect variations in materials of construction, engineering and technological inputs, and a wide range of other factors, so that apparently similar units may have widely different levels of reliability and durability.

NOTE: Reference to brand or company name does not constitute endorsement of any product by the consultant or UNIDO. Neither does such mention of company or product infer superiority or comparison with other products of a similar nature not mentioned.

II PRODUCTS AVAILABLE

Under each product sub-heading below are listed the reference numbers of suppliers able to offer such plant or equipment or alternates. The product and suppliers and reference numbers are cross-referenced at Section III A "Product/Supplier Index". Suppliers reference numbers may also be found under suppliers addresses. Section III B.

The sequence of equipment deal⁺ with below attempts to follow the normal pattern of effluent treatment, i.e. Screen - Primary Treatment - Secondary Treatment - Sludge; however, some items are used at many stages of effluent processing e.g. pumps, aerators etc., and for convenience these are covered jointly at the first possible employment in the sequence.

A. SCREENS

NOTE: In most cases it is preferred to screen effluents prior to pumping and/or equalizing, thus flow to screens will not be at equalized flow rates. Thus, given a small tannery of 50 hides/day which would produce some 50 m³/day, i.e. equalized flow of 2 m³/hour it is quite possible for a peak flow of 20 m³/hour rate be experienced for short periods (i.e. discharge of lime float for 50 hides x 25 Kg at 300% float = $4 \cdot 4$ m³ over a span of 15 minutes). Thus for screening purposes flows could be :-

Tannery	Daily Flow	Equalized Flow	Possible Peak Flow
50	50 m ³	$2 \text{ m}^3/\text{hour}$	$20 \text{ m}^3/\text{hour}$
300	^ر m 300	$12.5 \text{ m}^3/\text{hour}$	$100 \text{ m}^3/\text{hour}$
1,000	1,000 m ³	42 m ³ /hour	$200 \text{ m}^3/\text{hour}$
Potential	Suppliance Paf	Non 0/17/20/22/2	2/21./1.0/50/

53/64//90/103.

A. 1 GRIDS

GRIDS: designed to removed coarse objects, i.e. polythene bags, skins etc. for installation in developing countries with low labour costs may be locally fabricated and manually cleaned. For large projects or where labour costs are high, mechanically cleaned bar screens are available. A simplistic outline of such a rotary raked vertical bar screen may be seen at Fig. A (i). Slightly more sophisticated models are more normal with the rake attached to a chain and cog device, operating behind the bar screen. Width between bars may vary from 2 -10 cms. Channel width is the normal basic specification parameter. Range of channel widths normally 40 cms - 1.50 metre (10 cm steps).



TYPICAL BUDGET PRICES (Supplier Ref. No. 40)

Channel V	lidth	Motor HP		US \$
40 70 100 1,500	cms cms cms cms	0.5 0.75 1.00 1.50		2,136 2,708 3,219 4,061
Optional Torque Limiting Device =				220

A 2 SCREENS

Three broad categories of screens are availabe (with some degree of overlap).

a) SELF CLEAN SCREENS

Such screens are normally composed of "wedge wire" screen panels. In order to obtain the self cleaning properties wire spacing of correct dimensions is essential as is the correct dimensioning of the screen



panel to avoid blinding of the grid. The wire spacing is governed by the characteristics of the grid. But for many screens $1 \cdot 0$ -
1.5 mm is an acceptable range for tannery usage. A number of patented stainless steel "wedge wire" conformations are available - some yielding a high level of "self-clean" properties (some lower cost products of more basic design still require regular manual attention). Fig. A (ii) shows the typical layout of such self-clean screens.

Fecently a number of lower cost static screens have entered the market, these may have screens constructed of plastic materials, their design may not always yield full "self-clean" characteristics, but this is often partially overcome by adjusting the angle of the screening unit and the filter action may be augmented by fitting a vibrator (pneumatic or electric motive power).

For a variety of reasons the two types of screen are not readily comparable. The stainless wedge wire units are usually self-contained and may be installed easily and, if necessary, implanted within the floor, whereas the cheaper plastic screen units are simpler, free-standing models, not easily sunk into the ground



if the rake adjustment is to be employed. See Mg. A (iii).

The price span of available equipment is thus wide, some reflection of material and engineering inputs :-

Budget Prices

Stainless Steel - Self Clean				Static Plastic T	ypes
(Supplier Ref. No. 34) *				(Supplier Ref. 20)) **
Flow	<u>Dimen</u> Weir	sions Screen Length	<u>US \$</u>	Dimensions	<u>US</u> \$
20 m3/hr	0.6 m	1.2 m	2,321;	1 · 3 x 1 · 6 m	1,619
120 m3/hr	3.0 m	1.2 m	8,690	1 · 9 x 2 · 1 m	2,805
240 m3/hr	2 x 3.0 m	1.2 m	17,380	2 · 9 x 2 · 1 m	5,174

Complete stainless steel unit

Plastic Grill, stainless body, galvanised supports

May need an additional cost for vibrator of approximately 10 - 20% extra.

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(Self Clean Screens available in wide range of sizes - weir width available 0.5 m - 3.0 m by 0.3 m steps).

b) BRUSHED SCREENS

The brushed screen is possibly the most frequently employed screen used in tanneries. Universally known by its generic name "Parkwood" type, it has proven durability and, apart from infrequent but regular replacement of the polypropylene brushes, needs little attention. They are available with choice of perforation - 1.5 mm perforation often employed in tanneries. From the installation viewpoint they are simple to sink into the floor and require relatively little level fall.

Fig. A (iv) bialle TYPICAL BRUSHED SCREEN -End View balivery Balike Bereamed BETTIMEN Bistoryed via upon base.



Budget Prices :

	Brushed Screen	- Supplier Ref. No. ó4	* **
Capacity	Brush Motor	Screen Size	Budget Price
$29 m_3^{3/hr}$ 112 m_2/hr	0·375 Kw 0·75 Kw	0.8 long x 1.0 m wide 1.6 long x 1.9 m wide	US\$3,387 7,268
280 m ³ /hr	1-10 Kw	$3.9 \log x 1.9 m$ wide	12,141

* Stainless screen, mild steel body zinc coated then machine enamelled

** Spares set including bearings and brushes from US \$ 150 -350 per machine.

(Standard Brushed Screen unit available from 0.5 - 4.0 m long by steps of 0.4 m or similar).

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c) <u>ROTARY SCREENS</u>

A wide range of rotary screens are available. Fig. A (vi)

shows the side view of a typical model currently marketed. Generally the screens are of stainless steel - some screens employing perforations, others slots. Drive is variously by cog or chain



drive to drum screen periphery, or direct mounted motor. The more sophisticated and efficient drum screen have internal auger shaped integral conveyance systems, or other patented devices, to promote the discharge of the separated solids. Additionally, with such screens a cleaning device may be installed, employing brushes and sometimes, also, water jet spray.

Perforations suitable for tannery usage are circa 1.0 mm. The fall required by rotating drum screens is circa 0.5 metre. Typical Budget Prices (as Fig. A (vi) Supplier Ref. 90

Throughput	Unit	Drum Dimensions	Motor	Cost US \$
$5 m_{3}^{3}/hr$	1	mini unit	0·15 Kw	3,800
20 - 80 m_3/hr	1	0.6 dia. x 0.9 m	0·75 Kw	7,344
90 - 180 m ⁹ /hr	1	0.6 dia. x 1.9 m	1 · 10 Kw	9,934
80 - 300 m /hr	2	0.5 dia. x 1.8 m	2 x 1 · 10 K	w 19,857

A more simplistic system exists (possibly of a lower "self clean" nature) where the crude effluent is fed to the exterior of a rotating screen, with the cleaned effluent entering the rotating screen.

Budget Prices

(Supplier Ref. No. 20)

Flow	Drum Width	Cost US \$
$70 \text{ m}^3/\text{hr}$	0.4 m 0.7 m	4,693 5.247
250 m ³ /hr	1.0 m	6,185

B PUMPS – EFFLUENT

NOTE: The selection of pumps for effluent handling is most critical. It is assumed that a screened effluent - following equalization - will be pumped forward at a constant rate throughout 24 hours. It is also assumed that pump flow is governed by a level control device, as few pumps can withstand "dry pumping". It is further assumed that in general tannery effluent is not compatible with normal "non-return valve" operation, and for this reason some so-called "self priming" pumps which incorporate such valves may not be suitable in tanneries.

The three scales of tannery mentioned earlier i.e :

Small - 50 m^3 effluent/day will yield an equalized flow of circa $\frac{\text{m}^3/\text{hr}}{2\cdot0}$ Medium - 300 m^3 effluent/day will yield an equalized flow of circa $12\cdot5$ Large - 1000 m^3 effluent/day will yield an equalized flow of circa $42\cdot0$

In general it is inadvisable to attempt pumping even well screened tannery effluents through a pipe of less than 38 mm $(1\frac{1}{2}n)$ diameter, otherwise the risk of blockage may be great. Where possible pipes of 50 mm minimum are preferred. This poses problems for the small unit above, as even the output of the normal small commercially available pumps of 38 mm diameter far exceeds the rate of 2 m³/hour: in such circumstances it may be preferable to use a pump/pipe combination of excess capacity, but incorporate a time switch (e.g. 2 minutes on - 5 minutes off) in the pump circuits. Alternatively, the helicoidal pump or similar which may be more easily controlled, by motor speed adjustment, could be employed (see C Pumps, Alternatively, the employment of macerator pumps Sludge later). may allow smaller bore pumps to be employed. Care must be taken to ensure that the velocity through pipes is sufficient to ensure selfcleansing velocity of some 0.75 m/sec (i.e. minimum flow rate through pire of 65 mm is some 7.5 m³/hour), more normally flow rates approaching 3 m/sec may be preferred - but over velocities of 4 m/sec excessive scouring may occur.

A wide range of mounting arrangements are available for effluent pumping - the most common are :-

(i) <u>Submersed - Portable</u> Suitable for small units - a submersible pump is installed on the chamber tase, either flexible piping or quick release couplings will allow the pump to be easily removed for service etc.

- (ii) Submersed. Submersible pump is lowered to base of vessel employing guide rails and attached with a quick release coupling.
- The pump is situated in a "dry well" (iii) Dry Well. excavated adjacent to the chamber, so that the pump is positioned at lowest pumping level anticipated. The pump is connected via a pipe through chamber wall.
- Inlet via suction pipe. (Need (iv) Surface Mounted Pump. for self priming action).

The characteristics of pumps may vary from manufacturer to manufacturer and therefore typical performance curves given below (Potential supplier will supply his may not always be relevant. Capacity varies according to power input/ own performance data). A wide range of centrifugal pumps are motor RPM/head/pipe size etc. available for use - generally, considering the high risk of solid particles in tannery effluents, it is preferable to employ "unchokable" vortex or similar styles which have impeller chambers with high solid passing capacity.

Potential Suppliers: Ref. Nos.

1/1山/16/27/32/33/35/39/山山/ 47/51/69/71/72/81/87/101.

cost and trouble-free operation) with a turbine impeller and a patented cutter insert has performance curves as shown in Fig. B (1). As may be seen the output of even the smallest pump at, say, 5 m head (approximately 0.5 bar) exceeds the



requirement of small/medium tanneries (although flow could also be reduced by fitting a bypass to return some pumped liquor to the supply vessel).

Typical Budget Prices for such pumps :-

		SUBMERSIBLE PUMPS	
Pump	Kw	Supplier Ref. 39	Supplier Ref. 44
A B C D E	1 · 1 2 · 5 4 · 0 4 · 0 5 · 5	US \$ 1,063 1,115 1,211 1,201 1,342	us \$ 1,400 (2 HP) - -

Turbine Impeller with cutter

<u>-::</u>-

Full range available - only above non-clog unit priced includes control panel and two level regulators.

Lighter duty submersible pumps are available from a few suppliers and could prove suitable in small installations, (e.g. Guinard) models of 0.55 - 0.75 Kw with outputs of $5 - 7 \text{ m}^3$ /hour at 5 m head (according to impeller fitted) are available at US \$ 4 - 500.

A wider range of non-submersible centrifugal pumps may be employed in dry well installations or other situations where they can operate under positive suction head. Examples with technical detail, specification and Budget Prices may be seen :-

TORQUE FLOW - CENTRIFUGAL PUMPS (S/R No. 87)						
Installed Motor Power	Absorbed Power	Diameter Suction - Discharge	$\frac{m^3/hr^*}{}$	<u>US \$</u>		
1.5 нР 2.0 нР Ц.0 нР	0.4 - 0.5 HP 0.8 - 0.9 HP 2.1 - 2.3 HP	50 mm 32 mm 65 mm 40 mm 80 mm 65 mm	2 15 40	797 833 1,632		
* at 5 m head.						

C PUMPS - SLUDGE

The volume of sludge is dependent on the efficiency of the coagulation, flocculation and sedimentation received during primary

treatment. A typical sludge volume could be 8 - 101 of total effluent volume.

Thus the three tannery scales previously used as examples :-Small Tannery 50 m Effluent/day could yield 5 m_3^3 /day sludge Medium Tannery 300 m Effluent/day could yield 30 m_3^3 /day sludge Large Tannery 1,000 m Effluent/day could yield 100 m³/day sludge

The outputs of sludge pumps - employing a minimum of 50 mm (2") bore pipes - generally exceeds the continuous flow rates needed for the above volumes. It is quite normal for such pumps to be time clock operated to obtain a few minutes pumping every 1/4 or 1/2 an hour.

Potential Suppliers: Ref. Nos: 1/3/10/14/24/27/33/35/44/47/ 65/70/71/72/81/87/103

C. 1 HELICOIDAL PUMPS

These are the most commonly employed sludge pumps. The advantage of such pumps is that they are positive displacement, able to corvey solids and have a self-priming action. The output of such pumps is governed by diameter and eccentricity of the Rotor (and pitch of stator) which are characteristics of individual manufacturers' ranges, as well as by the viscosity of the liquor Thus the formulas involved in pump selection are being pumped. Fortunately the flow is proportional to the speed of complex. rotation and in practice adjustment of RPM is employed to obtain required output and manufacturers all are prepared to assist in It should be noted that helicoidal pumps must not be selection. allowed to run dry (Flcat Control essential if pumping from vessel Run Dry protection is installed in some not continuously filled). pumps operated by an electronic sensor and relay.

Some typical examples of Helicoidal Pumps, specification and Budget Price (including motor) may be seen : (Suppliers Ref. No. 47) *

Installed HP	<u>Flo</u>	w at RPM * 500	** <u>1,000</u>	<u>Pipe Diameter</u>	<u>Cost</u> ** <u>US \$</u>
1.5 2.0 3.0 5.0 7.5	0.8 m ³ /h 1.25 m ³ /h 2.6 m ³ /h 6.1 m ³ /h 11.6 m ³ /h	1.9 m ³ /h 2.8 m ³ /h 5.6 m ³ /h 13.0 m ³ /h 25.0 m ³ /h	$1 \cdot 0 = m^3/h$ $5 \cdot 0 = m^3/h$ $1 \cdot 3 = m^3/h$ $28 \cdot 0 = m^3/h$ $39 \cdot 0 = m^3/h$ (800 RPM)	38 mm (1 ¹ / ₂ " 63·5 mm (2") 63·5 mm (2") 76 mm (3") 101·6 mm (4")) 678 969 1,027 1,289 1,372

The Table quoted refers to Brazilian standard domestic prices -

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discounts may be obtainable for export.

- Body cast iron, rotor and shaft stainless steel. Pressures 6 Kg/cm² (Single Stage Pumps).
- ^{***} Intermediate speeds available in steps of 50 RPM. Flow rates assuming pressure of 2 Kg/cm².

(Slightly cheaper models may be obtained in other countries, e.g. somewhat similar specification to the 1.5 HP pump i.e. $4.0 \text{ m}^3/\text{hr}$ may be offered at circa US \$ 500).

C 2 PLUNGER PUMPS

May equally be employed for sludge pumping, although their major employment in the tannery sector is for pumping fleshings. Their output is possibly too high for small/medium tanneries, e.g. 3 HP, 7" plunger, 76 mm (3") pipe, has an output up to 9 m³/hr (at 3 m suction). (Supplier Ref. 81). Budget Price: US \$ 2,017

C 3 DOUBLE DISK TYPE

Diaphragm pumps, said to be suitable for slurries, and will accept solids up to 12 mm, in addition to being self-priming, such pumps are able to run dry without damage.

Typical output curves of such pumps may be seen at Fig. C (i).



Specification and Budget Prices for Double Disk Pumps may

be: (Supplier Ref. No. 71)

* Pump (See Fig.C (i)	Pipe Bore	Speed RPM	Installed HP	Approx. Output m /hour	Cost US \$
A	50 mm (2")	300	0.75	2	1,345
B	50 mm (2")	475	1.00	5	1,359
D	50 mm (2")	1,480	3.00	15	1,128
F	76 mm (3")	730	10.00	40	2,439

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** At 5 m head.

Pump Aluminium. Discs and Trunnions of high grade Nitrile

D DOSING PUMPS

Potential Suppliers: Ref. Nos: 8/12/16/37/46/55/84/85

Dosing Pumps are available operated by diaphragm or piston. The major differences being pressure and accuracy of discharge. Such dosing pumps may discharge into mixing vat or directly into the pumped effluent within a pipe. Given typical tannery usage either style may be applicable, as pressure requirements even when injecting into a typical pumped flow pipe is not unduly high.

Dosing Pumps are normally actuated and controlled by effluent flow pump circuit and also coupled to pH controller. Proportional dosing is available controllable by pH meter and/or flow meter, however, provided flow and pH are not unduly erratic such levels of sophistication may not be justified within tannery effluent operations. And it is more normal in developing countries to operate an "on-off" system, manually adjusting the 0 - 100% control of maximum flow normally available on these units.

Materials of construction of diaphragm and piston may vary according to reagent being dosed. It is essential, however, that the pump unit be sufficiently robust and corrosion proof. Pumps are available with 1, 2 or more dosing heads (each individually adjustable) operated by one motor.

S/Ref. No. 12* Diaphragms	S/Ref. No. Pistons	<u>46</u> ** <u>S/Ref No.</u>	84 84	<u>S/Ref No</u>	• <u>55</u>
Range US\$ 0 - 10 1/hr 611 0 - 100 1/hr 669 0 - 200 1/hr 697	$\begin{array}{rrrr} \frac{\text{Range}}{30 1/h} & \frac{10}{5} \\ 0 & -105 1/h & 6 \\ 0 & -190 1/h & 6 \end{array}$	IS\$ Range 593 - 608 0 - 120 1/h 583 0 - 500 1/h	<u>US\$</u> 61 3 735	0 - <u>Range</u> 0 - <u>30 l/h</u> 0 - 200 l/h	US\$ 425 - 1,000

Typical dosing ranges and budget prices may be seen :-

Liquid end of pump constructed stainless steel

Stainless Pump

Wide range of construction available. Budget Priced quotes material not specified.

Double Headed Dosing Pumps in general costing from 60 - 70% more than single units are available with the output of each pump being individually controllable (0 - 100\% of output).

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E SUBMERSED AERATORS

Potential Juppliers: Ref. Nos: 1/34/44/45/52

E 1 TURBINES - SELF ASPIRATING AND BLOWER AIDED

A typical submersed (immersed) aerator consists of a submersible motor coupled to a turbine rotor within a stator. The rotating turbine creates a vacuum which is filled with air entering through a snorkel pipe. The air and water are intimately mixed and discharged via diffuser channels to form bubbles in the reactor vessel. High rates of oxygen transfer are reported, and the turbulence keeps solids well suspended. The efficiency of such units increases with depth blowers may be employed to increase efficiency at depths of 4 m or more.

Two zones of activity are obtained:- The inner zone A in Fig. E (i) has high levels of aeration and turbulence, and is the area of maximum activity. The outer zone - B in Fig. E (i) has lesser levels of aeration, but still sufficient flow to allow mixing and ensure solids are kept in suspension.



Submersed aerators may be employed :-

<u>Stationary</u> - sitting on the base of the reactor vessel held by their own mass or positioned with guiderails which may be attached to a bridge,

Mobile - attached to moving or revolving bridges,

Floating Motor - with buoyancy chamber

In addition to relatively high oxygen transfer rates a major advantage of submersed aerators is their low noise level, which is reported to be below 35 decibels at 50 m discance. (Well below noise levels of typical surface aerators).

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Specification and Budget Prices of some Submersible Aerators may be seen :-

Motor Rating	<u>Activi</u>	*****ctivity ZonesOxygen Transfer RatesDimensionsSelf Aspirating		Cost	
<u>Kw</u>	Dir			US \$	
4•4 13•5 30•0	▲ metres 2•6 ↓•0 5•0	<u>B</u> metres 6.0 10.0 12.0	Basin A Kg/hr 5.0 22.0 45.0	Basin B Kg/hr 3.5 14.0 30.0	3,266 5,704 9,063

Supplier Ref. No. 45*

* Full range available with motors of 4.4/5.9/13.5/22/30/14/55 Kw
** See Fig. E (i) above for Zones A and B

Clean water, standard conditions at 4 - ó m depth.

Transfer of oxygen may be increased employing air blowers come 50% increase in the small units but only circa 20% extra transfer for the larger units $\mu\mu/55$ Kw.

Supplier Ref. No. 1

Pump Kr.	Max. Oxygen Input Kg/hr	Budget Price
6.5	4·5	3,659
11.6	7	5,289
25.0	22	16,066

Other immersible aerators are also available with Budget Prices as shown: It must be noted that specifications are not directly comparable, and

more detailed output curves are available from manufacturers.

E 2 CAVITATION AERATORS

These are reported as being most economical when employed in sulphide oxidation operations. They are small and relatively easy to install.

Typical Budget Price for a 1.1 Kw unit circa US \$ 2,550 (Supplier Reference Nc. 52). Reported transfer rates as high as 20 Kg Oxygen/hr at high sulphide concentration.

E 3 OTHERS

For small scale aeration operations, it is possible to employ Air

Ejectors coupled to submersible water pumps. The pumped water jet passes through a nozzle in the ejector housing; a partial vacuum is created, which causes air to be sucked via a snorkel of 2 m or so, such air is intensively mixed with the pumped water. Such units may transfer up to 10 litres air/sec, with oxygen transfer efficiencies of 10 - 25% according to depth of immersion (1 - 2 Kg oxygen/hour). Such ejectors cost of the order of US \$ 150 - 400 and require a submersible pump, possibly a further US \$ 250 - 400 (see earlier).

F AERATORS

Potential Suppliers: Ref. Nos: 4/6/16/22/23/34/36/37/40/49/94

Aerators are available in a number of styles :-<u>Surface Aerators</u> - on floats (high and low speeds available) <u>Surface Aerators</u> - supported on bridges (high and low speeds available) <u>Non Surface Aerators</u> - with motor mounted on bridge and impeller at fixed or adjustable immersion depth.

Aeration is effected by 4 or 6 or 8 bladed paddle arms (slow speed) or by 2 - 15 or more bladed propellers or inverted fluted integral cone impeller/rotors. Rotors are generally of stainless steel construction and with better units dynamically balanced (high speed). Floats normally of stainless steel or fibreglass foam filled.

High speed aerators are directly coupled to the motor - usually 950 or 1500 RPM, in large units 2 speed operation is available. Slow speed aerators with speeds of 40 - 80 RPM require reduction gear, may be more expensive. Oxygen transfer efficiencies do not vary greatly from type to type and selection of model is much influenced by the scale of the operation. For small/medium units floating aerators are more popular having negligible installation costs, with bridge type constructions only being employed for large units where the cost of the necessary structure is balanced by ease of access for servicing.

The operational characteristics of aerators vary from manufacturer to manufacturer, but a typical guide to operating depth of a high



speed aerator may be seen at Fig. F (i).

The dimensions of "Zone of Activity" for aerators vary, but typical tank dimensions (as quoted by an aerator supplier) may be seen :-

TYPICAL SPECIFICATION OF FLOATING AERATOR					
HP Oxygen Transfer ng O_/hour [*] Spray Diameter. Metres Mininum Tank Dimensions - Metres Maximum Tank Dimensions - Metres	2 3·3 4 3·5 7·0	5 7·5 4·6 5·5 10·0	10 14·5 5·5 8·0 16·0	20 25•4 6•5 10•0 20•0	40 1,5•5 8•0 14•0 27•0
*		3			

Measured with absorbed power of 30 w/m^3

TYPICAL CURRENT AERATOR BUDGET PRICES (in US \$) :-										
	Poten	Potential Suppliers Reference Nos :								
HP	4	23	36	37	40	40				
2 - 3 5 10 15 20	- 10,563 11,972 14,085	1,264 2,076 2,768 - -	6,338 8,451 - -	1,460 1,700 2,510 - -	1,955 2,467 3,159 3,670 4,152	2,016 2,316 2,918 3,430 3,971				
Floating (including Float) Fixed	¥	¥	*	*	¥	¥				
High/Low Speed	Low	Low	Low	High	Low	High				

NOTE :

Budget Prices above based on recent quotes but most manufacturers produce full range from 2 - 100 HP.

G. AIR BUBBLE DEVICES/DIFFUSERS

The basic operation of such devices entails an Air Blower (see Section H later), connected to one or more porous or perforated devices laid or fixed to the base of the reactor, which will cause air bubbles to rise to the surface, oxygenating as they rise, in addition to stirring the liquor.

Oxygen transfer is governed by the diffuser size, porosity, bubble size, immersion depth and loading. Transfer of oxygen is measured by the efficiency in relation to the oxygen available in the air being diffused. This varies from 20% or so with fine bubbles and declines to only 8 - 10% with coarse bubble systems. (1 m³ air holds some 0.285 Kg. Oxygen).

A wide range of porous materials may be employed for the diffuser:-Fused Aluminium Oxide, conglomerated granulated quartz, ceramics, sintered plastics. An equally wide range of shapes and sizes of diffuser are also available with the result that direct comparison of cost:efficiency is impossible. It must also be noted that the cost of the diffuser may only be a fraction of the total cost - the bulk of expenditure often being accountable to the network of piping and associated blover.

The sizing of diffuser/blower combinations must take due account of four components: hydrostatic pressure (water head), pipework losses, pressure drop through diffuser and necessary reserve.

Major advantages of diffused air systems are the low noise level (only the blowers produce noise, and this may be damped down by enclosing and insulating the unit), and the low running costo. Fig. G (i) shows some comparative capital: running costs of alternate large



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scale systems (published by a diffuser producer 1977). With the increase in power costs the differences today may be appreciably more marked.

Potential Suppliers: Ref. Nos:

25/28/35/36/40/41/42/ 53/56/74/82/89/103

G 1 POROUS DIFFUSERS (Conglomerated/Fused Materials and Sinters)

a) TUBE

These are available in a wide range of sizes from 40 - 70 mm diameter, in lengths of 500 - 1,000 mm. Common practice is to

2 x 500 mm tubes to the main supply pipe = 1 metre of diffuser. A network of such diffusers may then be easily built up as shown at Fig. G (ii). Normal output of such diffusers 50 mm 0.D. with pore size 40 microns -Fine Bubble = 10 - 20 m³/hr/m of air diffuser.

affix, opposite each other,



Oxygen transfer efficiency varies according to depth of immersion and flow rates. Typically :-

	2 m depth	-	15% efficiency
increasing to	8 m depth	-	50% efficiency

declining to

Minimum Air Flow of Diffuser -33% efficiency Maximum Air Flow of Diffuser -20% efficiency

Pressure loss due to air resistance of the diffuser is reported at 25 - 30 mbars, but manufacturers suggest 80 - 100 mbars should be allowed when calculating blower requirements. (Variation in specification affect both output and pressure loss). <u>Eudget Costs : US \$ 40 - 60</u> per meter diffuser (including connectors) (Large volume discounts available) Budget prices refer to 100 units.

b) DONE/PLATE/CANDLES

The porous materials mentioned above are available in a wide range of shapes and configurations, some examples may be seen :-

(i) <u>Plate Diffuser</u> - 360 mm. diameter - output
 5 - 10 m³/hr - Pressure drop up to 50 mbar
 dependent on Air Input (see above) (for fixing
 to distributor pipe network).

S/Ref	89	Circa	<u>US</u> \$	28	each c	:omplet	te		
S/Ref	41	12" x	12"	- Ci	rca US	5 \$ 18	diffuser	plate	only

- (ii) <u>Plate Diffuser</u> 260 mm. diameter output normal 5 6 m³/hr. Pressure drop up to 30 mbars. Spring loaded plate to minimise baciflow.
- S/Ref 25 Circa US \$ 28 each complete
 - (iii) Dome Diffusers -17.8 cm. diameter Fused Aluminium Oxide Dome welded and fused at 12" centres to
 4" PVC distributor pipe output 1 2 m m³/hr.
 Fine 2 mm bubbles

S/Ref 53/74 Approximately US \$ 21 each dome (Price includes pipe).

G 2 LIFTING COVER - NON-CLOG DIFFUSERS

The most popular of these consists of a cone shaped plastic base fitted with elastomer cover which lifts around the edges to allow escape of air. When air pressure is reduced the cover returns preventing backflow.

Typical product - 12.5 cm diameter output 10 - 15 m³/hr, (Bubble size not quoted). (May be larger and less efficient than porous diffusers reviewed earlier). Pressure drop circa 30 mbars. Budget Frice (Supplier Ref. 35) Circa US \$ 16 each

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G 3 FOROUS PLASTIC TUBING

A wide range of easily installed porous plastic diffuser tubing is now available, which may be laid snake-like on the vessel floor from a main distributor pipe. A typical 18 mm. diameter tube with pores of 10 - 100 u is said to discharge $2 \cdot 4 \text{ m}^3 \text{ air/hr/m length}$ with a feed pressure of 0.5 bar. Such tubing may not have individual lengths exceeding 7 metres.

Budget Price: (Suppliers Ref. No. 56) US \$ 2.3 per meter (coils of 50 or 100 m).

G 4 LARGE BUBBLE PRODUCERS

A recent innovation has been the perforated plastic drum type diffusers. These units need ballast to overcome bouyancy. The 12 - 25 mm holes produce a high volume of coarse bubbles yielding relatively low levels of oxygen transfer efficiency. Their advantage is ease of installation with one unit handling high volume of air output. A typical example - The Venturator - 1 diffuser can have an output of up to 82 m^3 air/hr. The low efficiency is such that up to 180 m³ air is required per Kg/B.O.D._c at 3 m. depth; this apparent inefficiency is partially balanced by the large volume handled. Such air flow is ideal for dispersing suspended solids. 1 unit is said to be able to agitate a tank of 3.9 m x 3.9 m x 3 m deep.

<u>Budget Price</u> (Suppliers Ref. No. 103) <u>Circa US \$ 220 each</u>, including flexible hose fitting.

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NOTE: (1) The choice of fine vs coarse bubble aeration devices should not be based on capital cost alone. Fine bubble porous diffusers may become blocked if heavy concentrations of lime are present and if air flow is cut off. The presence of detergents may also reduce the efficiency of fine bubble diffusers. Under good conditions fine bubble diffusers may have an aeration efficiency of $l_{1} \cdot 0$ Kg oxygen/KwHr, as opposed to the $1 \cdot 0 - 1 \cdot 2$ Kg/KwHr for coarse bubble operations. NOTE: (ii) The oxygen transfer efficiencies reported above refer to clean water. With high levels of pollution e.g. Sulphide bearing Lime liquors the efficiency will be appreciably higher due to their avidity for oxygen.

H AIR BLOWERS

Potential Suppliers: Ref Nos: 18/26/80/87/92/98/103/105

The volume of air required for any treatment process will be governed by the degree of efficiency of the diffusion system. With transfer efficiencies ranging from 25% (fine bubble, deep tank) ie 25% of 285 gms oxygen/m³/air = 71 gms oxygen/m³ air = $14 \text{ m}^3 \text{ air} = 1 \text{ Kg oxygen}$ to low efficiency (coarse bubble) operation requiring 180 m³ air = 1 Kg oxygen.

Thus, assuming 1 Kg oxygen = 1 Kg B.O.D.₅ the three hypothetical tanneries outlined earlier, with an efficient primary treatment yielding an influent to a secondary treatment system of circa 500 mg/litre B.O.D_c could require:

			Air Requirement Efficiency			
	m ³ /day	BOD _c /day	High m ³	$/d m^3/hr$	Low m^3/d	m ³ /hr
Small Tannery Medium Tannery Large Tannery	50 300 1,000	25 Kg 150 Kg 500 Kg	350 2,100 7,000	(15) (87) (292)	4,500 m ³ 27,000 m ³ 90,000 m ³	(187) (1,125) (3,750)

To cover this wide span of possible requirements and allow reserve capacity, it was felt expedient to seek budget prices of blowers of $50 - 200 - 2,000 - 8,000 \text{ m}^3/\text{hour output at a differential}$ pressure of some 300 mbars. (Intermediate prices available by extrapolation.)

In general it may be noted that the Roots/Positive Displacement blowers are appreciably cheaper than the centrifugal blowers. Budget Prices and specifications for varying sized units may be seen :-

NOMINAL	OUTPUT	-	AIR	BLOWERS

		50 m	³ /hr	200) m ³ /hr	2,000	0 m ³ /hr	8,00	0 m ³ /hr
<u>Suppliers</u> Ref. No:	Note	Cost US \$	Motor Rating	Cost US \$	Motor Rating	Cost US \$	Motor Rating	Cost US \$	Motor Rating
18 26 26 80 87 87 103	(1) (1) (2) (3) (4)(5) (6)	N/av " 882 805 95 N/av	railable " 0.8 kw 2.2 kw 1.3 kw railable	2,745 5,592 N/avai 918 831 137 3,380	5.5kw 1able 2.5kw 5.5kw 4.1kw 7.5kw	11,038 9,802 11,830 1,979 2,836 958 8,732	37kw 20•9kw 30kw 25kw 45kw	16,730 18,239 18,592 9,868 7,931 3,山9 28,296	110 kw 81•1kw 110 kw 91 kw 150 kw

Notes: (1) Multi-stage centrifugal Blower

(2) Roots Blowers

(3)	Prices quoted "Bare Shaft" - Positive Displacement						
	Air Blowers output quoted against 300 mbar pressure.						
	Kw = Absorbed Power						

- (4) Positive Displacement Rotary Blowers bare shaft output at 350 mbar differential pressure. Installed power.
- (5) Outputs not as table capacity, i.e. $200 = 430 \text{ m}_3^3/\text{hr}$ $2,000 = 2,550 \text{ m}_3^3/\text{hr}$ $8,000 = 4,250 \text{ m}_3^3/\text{hr}$
 - Motor for above. (Absorbed Power).

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I LEVEL CONTROL REGULATORS

(6)

Level control regulation, connected to flow pumps, is an essential of virtually every effluent treatment plant, to overcome the imbalance between influent rate and pumping rate. Thus, level regulation is necessary when low level is obtained to avoid "dry pumping" with danger to pump and, at high level, to avoid overfill.

To withstand the pressure of solids and the corrosive nature of tannery effluent it is normal to employ liquid level regulators comprising a mercury switch which is actuated by tilting, housed in a polyproylene bulb, similar units may be employed for the "high" and "low" duties with adjusted wiring.

Although many level regulators may operate at up to 380 v 10 amps and as such may directly activate small pumps, for heavier power control, an electric level control unit containing a relay is employed. In many countries electricity/safety regulations insist that only low voltage circuits be fed via level regulators, in such case the use of a relay circuit is essential, allowing the regulator to carry a 20 - 24 volt input with the relay/control circuits being capable of switching up to 4 ± 0 volts.

Potential Suppliers: Ref. Nos: 14/14/44/59 (a multitude of local manufacturers exist, in addition to these renowned international manufacturers).

Typical Specification and Budget Prices may be seen :-

- 1. <u>Level Regulator</u>
 - (i) Supplier Ref: 14 Standard unit Level Regulator, suitable for S.G. 0.95 to 1.10/up to 50°C/380 volt 10A or 250 volt 5A. Shock proof Mercury Switch cased in polypropylene.

Budget Price US \$ 55 (20 m lead)

(ii) <u>Supplier Ref. 14</u> - Similar to above, maximum working temp to 60°C, breaking capacity 10A @ 25C v.

Budget Price US \$ 43 (20 m lead)

 (iii) <u>Supplier Ref. 14</u> - Ultra heavy duty - switch encased in aluminium inner shell and totally vulcanized in rubber. 10A 250 v.

Budget Price US \$ 65 (20 m lead)

(iv) Supplier Ref. 144 - Light duty/clean water operation only, micro switch (single pole, double throw) polypropylene encased. May be employed to obtain switching with levels approximately 1.5 m level differential. Possibly only employable following efficient sedimentation.

Budget Price US \$ 21 (5 m cable)

2 Level Control Units

Typical units available :-

(i) Supplier Ref. 44 - Weatherproof plastic case includes

transformer to supply 24 v D.C. for level regulator to switch up to 440 v @ 3 amps. Budget Price US \$ 31

3 More Sophisticated Units

A wide range of systems are available employing sensors and electrodes. Some units can be obtained at relatively low cost, one such system with no moving parts and said to be suitable for use in sewage, employs continuous monitoring of the electrical resistance between an electrode and a return earth (another electrode or earthed installation itself). Such system may be applicable to effluent not liable to encrust the electrodes.

(i)	Supplier Ref. 51 -	Budget Prices:
	Basic controller, single trip	US\$85
<u>or</u>	With increased trips to	180
+	Housing basic	22
or	With up to 4 lights	69
+	Electrodes waterproof	75
or	Up to maximum length 4.5 m	235

(i.e. Total unit cost varies from US \$ 182 - US \$ 484 according to specification).

More sophisticated units are available, but their employment in developing countries may not be recommended as the necessarily high level of servicing may not be on hand.

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J pH CONTROLLER

Potential Suppliers: Ref. Nos: 37/55/73/84/91

pH controllers are essentially employed to activate dosing pumps or solenoid valves, adding acid or alkali as necessary. Conditions of good coagulation and flocculation vary from plant to plant and according to the reagents employed. It may be found in practice (trial and error) that good sedimentation is yielded between pH 8 and pH 9.5 (for example), outside this zone additions of alkali or acid may be necessitated.

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The range of suitable industrial pH controllers on world markets is fairly limited and standard. The total complete unit consists of a robust dip electrode (usually offered in $\cdot 45$, $\cdot 90$ or $1 \cdot 8$ m length) connected by coaxial cable to the pH controller. Such controller is housed in a weathertight container and contains provision to adjust 1 or 2 high-low points, at which pumps or valves will be activated or deactivated. In most cases the switching of low power-driven devices is direct, if heavy switching is required, a relay may need to be employed. On some units the high and low settings may be shown on digital readouts - on others such setting is only adjustable via uncalibrated knurled knobs.

The standardisation of the unit is similar to laboratory pH meters employing standard buffer solutions. Temperature adjustment may be manual or by automatic sensor.

Specifications and Budget Prices :-

(i)	Supplier Ref. No. 91	-	Budget	Prices
	pH controller - 2 set points pH 0 - 14. Relay contacts 6	over full range amps at 220 v	US \$	376
+	Combination Electrode			60
+	Electrode Sleeve 800 mm with	KCl reservoir		63
		Total	US \$	499
(ii)	Supplier Ref. No. 84. As 5 amp at 240 v auto temp. con internal "self test" facility etc.	above, outputs trol available, for calibration	<u>US</u> \$	458
	Electrode unit complete with reservoir	visible KCl	<u>US \$</u>	114
		Total	US \$	572
(111)	Supplier Ref. No. 37 - Comp specified	lete unit not	US \$ 2	,380*
(iv)	Supplier Ref. No. 55 - Comp specified	lete unit nor	US \$ 2	• , 700 [*]
¥	Domestic prices - Export pric	e may be considera	bl y red u	iced.

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K FLOW METERS

Potential Suppliers: Ref. Nos:

13/19/21/29/35/59/68/ 82/91/97/102

The need for effluent flow meters is questionable in small operations - it may be sufficient to meter the incoming clean water to the tannery as a fair guide to effluent volume. For larger treatment plants which may have prescribed discharge rates by local authorities or need to control the flow:reagent additions closely, metering may be considered desirable.

The cheap (varying from US \$ 150 - 50 mm pipe - US \$ 250 -100 mm pipe) simplistic "in-line" physical flow recorders impeller or piston operated, are seldom suitable for effluent treatment control, as such units are not normally designed for liquids with suspended solids.

Modern technology has produced a number of systems employing non or semi-intrusive devices employing ultrasonic, doppler or magnetic signals to measure depth of liquor - flow rate. Usually some degree of standardisation of condition i.e. need long run of straight pipe, or weir or flume of known characteristics in predetermined channel. Others may be calibrated on site and the more recent models include programmed microprocessors which may rapidly calculate flow parameters. Some units e.g. Sonic type open channel sensors will not function well in the presence of high foam. With the large number of unit types available a brief review only of typical types and budget prices is given, in order of increasing cost, of basic unit. below :-

 (i) <u>Supplier No. 91</u> - suitable for flow on calibrated weirs or open Venturimetric canals - air blowing system with mini compressor. Flow ranges 0 - 50/0 - 100/0 - 200 m³/hr, with total flow

Budget Price

US \$ 722

 (ii) <u>Supplier Ref. No. 21</u> - Semi-intrusive sensor (with impeller) for insertion into pipe - calibratable digital display unit (only requires pipe size entering). Flow and total display

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in CFM or m³/hr.

Wide range.

Budget Frice

US \$ 986

Budget Price	Standard Unit Optional Chart Recorders	<u>US \$ 1,676</u> <u>190</u>
	(Portable Model)	(2,338)

 (iv) <u>Supplier Ref. No. 19</u> - Clamp on pipe type flowmeter employing Doppler Transmitter/Receiver. Suitable for pipes above 18 mm O.D. (wall thickness up to 25 mm). Flow display - totals etc. and alarms.

Budget Price

US \$ 2,819

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L AGITATORS

Within tannery effluent treatment operation mixing may be required at several stages :

- (i) During homogenization/equalization this is now more normally achieved employing air diffusers or surface aerators;
- (ii) During addition of neutralizing, flocculating and/or coagulating agents. When polyelectrolytes are employed it may be preferable to employ low speed mixer/flocculators (see next section). Where acid/alkali additions are made, usually into mixing vats, it is possible to employ cheaper high speed mixers. High speed agitators with impeller directly fixed to motor shaft are relatively cheap, whereas slow speed and variable speed units, requiring gearing, are both larger and more expensive.

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The sizing and balancing of mixer/vat size is complex and the formulas necessitate factors relating to characteristics of the impeller, e.g. number/shape/pitch. To overcome this, most manufacturers issue their own performance charts. A typical relationship may be seen :-

Volume to be Mixed	HP of Agitat	Blade Diameter	
<u>m</u> ³	Gentle Agitation	Rapid Agitation	mm
0.2 - 0.4	0•05 HP	0•33 HP	100
0.4 - 0.7	0•15 HP	0.50 HP	100
0.7 - 1.5	0•25 HP	0.75 HP	100
1.5 - 2.2	0•33 HP	1.00 HP	100
2.2 - 3.7	0-50 HP	1•50 H₽	150
3•7 - 5•6	0•75 HP	2.00 HP	150

Typical Budget Prices from an European specialist producer (Supplier Ref. No. 43)^{*}

HP	RPM	ligh Speed Prope	Reduced Drive Speed			
	<u> </u>	TTOP: DIAM.	<u>00 q</u>	<u> </u>	TTOP. DIAM.	00 4
0.25	1500	100 mm	3 97 ·	462	150 mm	699
0.50	1500	100 mm	430	462	200 mm	756
1.00	1500	125 🛲	566	462	250 mm	982
2.00	1500	150 mm	601	46?	300 mm	1,231
5.00	1500	200 mm	800	462	450 mm	1,869

Fixed mounted heavy duty couplings, shafts and propeller in stainless steel. Motors TEFC Weatherproof.

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	Typical Sc	outh American	Producers	' Budget Pric	ce	
нр	RPM	Supplier Re Prop. Diam.	f. No. 55 US \$		Suppl: RPM	Ler Ref 37 <u>US \$</u>
0·3 1·0 5·0	1100/1200 1100/1200 1100/1200	100 mm 175 mm 250 mm	250 400 1,950	Portable Portabla Fixed	300 300 -	1,256 1,327 -

<u>Note:</u> 1 To avoid vortexing (mass swirling) it is necessary to mount agitators off centre and/or at an angle with the vertical. (Unless baffles are fitted to mixing vessel).

<u>Note:</u> 2 The number of producers of agitators is too large to attempt listing potential suppliers.

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M FLOCCULATORS

The simplest flocculators consist of slow rotating vertical wooden paddles as Fig. M (i).

Two or four arms may be employed with from 2 - 4 paddles per arm. The sizing of flocculators is difficult and it is normal to rely on manufacturers' specification. The Table below shows a specific manufacturer's suggestions for paddle sizes. 20 -



30 mins is normal time for flocculating, therefore the tank size will have a volume equal of 1/3 or 1/2 of hourly flow rate.

Utilizable Tank Volume m3	<u>Total</u> Width m	Tank Size Depth m	<u>Paddl</u> Height	<u>e</u> Dia.m	HP	Arms No.	Paddle No.per arm	Paddle RPM
6 12 20 16 - 25 30 - 50 50 - 80	2 2•5 2•5	1 • 9 2 • 4 3 • 9 3 • 9 3 • 9 3 • 9	1.05 1.55 3.05 3.20 3.20 3.20 3.20	1 • 6 2 • 0 2 • 0 2 • 0 2 • 8 3 • 6	0.75 0.75 0.75 0.75 1.50 2.00	2 2 2 4 4	2 2 2 3 4	4 - 8 3 - 6 3 - 6 2 5 - 5 2 - 4 1 8 - 3 5

Due to the wide variation in price due to materials of construction/methods of speed reduction etc. there is little purpose in listing Budget Prices. It may however be noted that employing the above data such slow moving flocculators may in many cases be assembled locally, with the majority of cost being attributable to the motor and reduction assembly.

N SEDIMENTATORS

The basic sedimentator is employed :

 (i) To separate flocculated suspended solids during primary treatment;

- (ii) To separate activated sludge, and allow its recycling, during secondary biological treatment;
- (iii) To thicken, i.e. remove further quantities of water from sludges formed at (i) and (ii) above.

The dimensioning of sedimentation units is usually calculated on the upward flow rate within the sedimentation unit. This may vary from 1.0 to $1.5 \text{ m}^3/\text{m}^2/\text{hr}$ for primary sedimentation following physico-chemical treatment, down to only $0.5 \text{ m}^3/\text{m}^2/\text{hr}$ for some secondary sedimentation.

For small operations requiring vessels of up to 3 or 4 m diameter, the simple vertical flow sedimentation tank at Fig. N (i) may suffice. Such units may be locally produced - circular in 6 mm plate (Fibreglass skinned internally or epoxy resin coated) or in reinforced



fibreglass, concrete or wood, dependant on local technology.

Typical Budget Prices for 6 mm steel plate units have been :-

<u>Cyli</u> Diam.	<u>nder Size</u> <u>Height</u>	<u>Surface Area</u> m ²	Flow Rate m ³ /hr	<u>Cost US \$</u>
1 m	3 m	0.8	0.5 - 1.5	1,500
2 m	3 m	3.1	1.5 - 4.5	3,000
4 m	3 m	12-6	6.0 - 19.0	5,000

For larger operations commercial models are available with rotating rakes with half or full bridges for access. Scum removers are also available, (see Fig. N (ii)). Central entry is common practice but some designers prefer the peripheral feed (Fig. N (iii)) as this limits the dispersion of scum and may be more stable with respect to high peak and fluctuating loads. It must be stressed that the large units are very expensive to transport, and it may be preferable to import in semi-fabricated form or produce locally under licence from experienced producers.



Some recent Budget

Prices of	Circular	Sedimentators	- (Clarifiers	:-
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	CLARIFIERS	(Cost in US \$ Ex Works)			
Diameter	Radial Bridge ⁽¹ Supplier Raf. 23) Single Arm ⁽¹⁾ Supplier Ref.40	Full Bridge ⁽²⁾ Supplier Ref. 23		
6 m 10 m 20 m	5,700 6,700 12,050	4,723 5,700 10,800	8,000 9,500 18,350		

(1) Peripheral drive, including scraper and skimmer

(2) Full bridge peripheral drive, including scraper and skimmer.

Clarifiers are also available in rectangular form, with "to and from" type scrapers.



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0 OXIDATION DITCH ROTORS

1 CONVENTIONAL DITCH ROTORS - BRUSH/CAGE/TNO etc.

Oxidation rotors are available in several styles, sizes, speeds and diameter of rotor with consequential variation in oxygenating capacity. Such oxygen transfer is further varied by the depth of immersion. Some manufactuers' oxygen transfer rates may only be applicable at high levels of B.O.D. when oxygen demand and efficiency is high. Some typical manufacturers report :-

<u>0.7 m diameter rotor</u>						
Rotor Immersion	Oxygen transfer Kg per hour per m length	Power Consumption <u>Kw/m</u>	Oxygen Capacity per unit power Kg/KwHr			
0·05 0·15 0·25	2 · 00 4 · 00 7 · 00	0-8 1-8 3-4	2 • 5 2 • 2 2 • 1			

1.07 m diameter rotor

Immersion	RPM	Oxygen Transfer per hour
		per m Length
·125	54	1.7
•380	72	10.0

Given the wide range of reported outputs and efficiencies it may be more realistic to take account of manufacturers' sizing. One manufacturer recommends for domestic effluents :-

Load Lg BOD/day	Length m	otor Diameter	Volume m	tch Length m	Depth	Installed HP
27.5	1 · 0	0 · 70	1 31	32	1.0 m	3.0
55.0	2 · 0	0 · 70	262	37	1.2 m	5.5
130.0	4 · 5	0 · 70	650	144	1.4 m	10.0
275.0	4 · 5	1 · 00	1 310	54	2.25m	20.0
550.0	6 · 0	↓ 1 · 00	2620	61	3.0 m	40.0

(Interim loadings available)

Such data may need modification to suit the concentration of pollutants/volume of ditch more suitable to tannery operation where two days retention in oxidation ditches seems satisfactory. In many circumstances two or more rotors will be necessitated. The

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rotor in addition to supplying oxyger. requirement must also supply the necessary hydraulic flow and most reputable manufacturers will supply ditch parameters to match given effluent characteristics.

Typical Budget Prices :-

(i) Supplier Ref. No. 55	US \$ Cost
0.9 m length x 0.7 m diameter Rotor - 3 HP 2.1 m length x 0.7 m diameter Rotor - 7.5 HP	4,900 6,500
2 x 3.6 m length x 0.7 m diameter Rotor - 25 HP	10,800

(ii) In response to a specific query regarding tannery

effluent one Supplier Ref. 103 quoted Budget Prices:-

Kg BOD5/day	Rotor	Diameter m	Installed HP	Cost US \$
50	1 х 2 m	0·7 <mark>**</mark>	4	6,338
300	1 х 4.5 m	1·0 <mark>**</mark>	22	19,155
1,000	2 х 7.5 m	1·0	37	47,042

Including drive - bridge - splashguard

** Mammoth rotors with rows of blades, non-horizontal, to avoid pulsating flow. Price excluding bridge and walkway.

Note: Rotors normally available from 0.75 or 1 m to 4 or 8 metres long in steps of 0.5 m.

Potential Suppliers: Ref. Nos: 55/62/63/103

O 2 BIO DRUM

A recent entrant to the market has been the Bio Drum a ".... rotating biological filter, where instead of plates the filter consists of a lot of plastic balls held together in the shape of a drum by a sturdy metal net. This new construction gives the advantage that the drums can float due to the very low specific gravity of the balls.

As at the same time small containers are built into the periphery of the drums and these containers lift water out of the water body and pour it over the balls in the upper section, this actually makes the drums a combination of rotating filters and trickling filters. As the same containers also trap air which is taken down in the water and bubbling up between the balls overgrown with biofilm the lower part of the drum is also a sort of submerged filter with air bubbling through direct along the surface of the biofilm.

As the drums are freely floating on the water to be treated, they can be mounted in any tank with a minimum of construction work, and they are therefore very well fitted for upgrading existing tanks simply mounting the drums at the edge of the tank by means of a pivot." (Manufacturers description).

Whether such units may operate at maximum efficiency in tannery employment is unknown to the consultant. Such drums are available in sizes from $0.625 \ge 0.4$ m up to $2.5 \ge 2.5$ m.

Manufacturers specification based on population equivalents is given below (B.O.D., load assumed by the consultant) :-

Population Equivalent	BOD5 Kg/day	Bio Drum Size m	HP Installed	<u>Cost US \$</u>
200 - 500	11 - 27	1 • 5 x 1 • 5	1	9,073
400 -1,000	22 - 55	2 • 0 x 2 • 0	2	12,600
700 -1,500	38 - 82	2 • 5 x 2 • 5	3	15,129

Supplier Ref. No. 38

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P BIO FILTER DISTRIBUTORS

Potential Suppliers: Ref. Nos: 15/16/22/27/37/40/67/103

The simplest systems are those which utilize the pressure of the pumped effluent to rotate the distributor arm. (Somewhat similar to rotary lawn sprayers). More sophisticated units may employ a motor to ensure regular rotation. Wide variations exist in materials of construction and it is difficult to compare prices.

Some typical Budget Prices: -

(i) Supplier Ref. No. 15 :-

2 r	netre	diameter	US \$	560)	Monoje t, central self
5	11	n	US\$	915)	dosing distributor.
9	11	n	US \$	1,408)	Supported on transverse
						bearers.

(ii)	Supplier Ref. No. 40					
	lı metre diameter 10 " "	US \$	1,805 3,008)))	Heavy duty centrally mounted, multi- diffuser arms.	

(iii) <u>Supplier Ref. No. 37</u> 4 metre diameter US \$ 580

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Q BIOLOGICAL (TRICKLING) FILTER - PACKING MATERIALS

The major characteristics of packing material for biological filters are : (i) Large surface area availability;

(ii) Sufficient voids to allow adequate air flow to ensure aerobic conditions.

Filters are available, or may be constructed to operate in several fashions :-

	Low Rate Filter	High Rate Filter	Roughing Filter
Hydraulic Loading m ³ /m ² /day	2 - 4	10 - 30	>50
Organic Loading Kg BOD/m ³ /day	0.1 - 0.3	0•3 - 1•0	> 1∙0
Media	Rock, Slag	R & S & Plastic	Plastic

Typical material characteristics :-

	<u>Diameter</u>	Kg per m ³	g per m ³ Area m ² /m ³	
River Pebbles	25 - 60	Circa 1,300	Circa 60	50 %
River Rocks	80 - 120	" 900	n 45	50 %
Furnace Slag	50 - 100	" 900	n 60	50 %
Plastic	-	30 - 100	n 90	95 %

Rocks and slag are usually available at nominal cost locally but it may prove economic to investigate the employment of plastic packing. As well as reportedly offering higher raise of loading, plastic media, due to its light weight may require a simpler, smaller, lower cost filter construction, with only a light structure to support the media. Additionally, plastic materials with their

-130-

high voids readily allow air circulation. Plastic Media is available in modular form or as a random media structure. The random structure would appear suitable. Such random media is available, usually under registered or patented design, as cylinders composed of ridged rings, typically 3 - 10 cm long with similar diameters. Alternately, materials are available composed of triangular serrated fins radiating from a central tube. Typically such materials are constructed of PVC.

Budget Prices :

- (i) <u>Supplier Ref. No. 96</u> "Flocor R" US \$ 80 95 m³
- (ii) Supplier Ref. No. 56 "Biofill" US \$ 85 m³

(Prices above for 20 m³ - higher volume discounts available).

NOTE: Freight costs of this bulky material may exceed actual material cost.

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R FLOTATION UNITS

Flotation units are an alternative to physico-chemical sedimentation systems. The process involves floating suspended solids to a

vessel's surface from where they may be scraped off of the liquor and collected. An outline of the basic system may be seen at Fig. R (i). The operation is based on the change in solubility of gas in liquids as pressure changes. Air is



dissolved in the waste stream under pressure in a saturation vessel which is then passed to the non-pressurized reactor vessel where micro air bubbles form, rise to the surface carrying with them the suspended solids forming a scum which is mechanically scraped. A discharge point at the base may also be necessary for the collection of ultra heavy particles. A variety of patented atomizers are employed to ensure fine dispersion of the bubbles. Patent screens and separators may also be employed for the baffle plate. In addition to the above dissolved air flotation (DAF) other flotation methods are available e.g. electrolytic flotation, but this seems not to have gained acceptance in treating tannery effluent, due to the high cost of transformer/rectifier.

The advantage of flotation is said to be that retention time in the unit is only some 45 minutes, versus up to 3 hours in a conventional sedimentation system. It is also reported that the solids content of the scraped sludge is of the order of 8 - 10%as opposed to the 3 - 4% obtained by sedimentation.

It must also be noted that even with flotation it is often necessary to neutralize or otherwise dose the influent.

Flotation equipment is usually sold as a complete unit. Potential Suppliers: Ref. Nos: 7/16/22/34/35/36/60/77/93

Typical Budget Price :

- (i) <u>Supplier Ref. Nc. 7</u> Complete Unit - 4 m₃³/hr US \$ 12,300 " " 90 m /hr US \$ 105,000
- (ii) <u>Supplier Ref. No. 93</u> A tannery developed a system for its own effluent treatment plant, found it successful and is now offering to supply such complete "Silflo" units:

This plant is complete with the necessary dosing facilities and is said to remove > 99% of S.Solids, chrome and grease and some 90 - 95% reduction of C.O.D. and B.O.D.

Cost of treatment employing the Silflo units was reported⁽¹⁾

(1)

ROET. S. "The Development of a Modified Flotation System for the Treatment of Tannery Wastes". ALCA Convention. June ,983. Hershey USA.

for a tannery of $125,000 \text{ m}^3/\text{year} (500 \text{ m}^3/\text{day}):-$

Capital (Amortized 15 yrs) + Interest (10%)	6.4 c m ³
Dosing (Ferrichloride + Polymer)	9.1 c m ³
Power (Silflo only) (15 Kw x 13.5 hrs daily)	1.7 c m ₂
Labour	7.3 cm ²
Maintenance (2% of Capital)	$0.13 c m_{2}^{3}$
Sludge Disposal (Landfill)	2.50 cm ³

Total Capital and Running Costs 27.13 US Cents m³

S FILTER PRESS

Potential Suppliers: Ref. Nos: 16/27/31/54/60/65/78/86/88

1. Sizing

Exact volumes of sludge and subsequent cake are difficult to calculate prior to operation. For an outline guide to allow sizing of Filter Presses, the following may suffice:

a) From Suspended Solids - i.e. 300 m³ effluent/day at, say, 3,000 mg/l S.S. would yield some 900 Kg day dry solids (D.S.)

b) From B.O.D. - subsequently precipitated and settled and from coagulants and flocculant added another 20% or so on the above may be produced.

c) Total may be 1,080 Kg - <u>say 1.1 mt</u>. D.S.

At 4% solids content (i.e. after primary sedimentation) this could occupy some 27.5 m^3 . Following a filter press operation a dry solids content of 30 - 35% could be obtained. Assume, say, 32% D.S. and a cake of some 3.44 m^3 could be expected daily.

The output of filter presses is governed by plate size, number of plates and thickness of cake. The nominal output is easily calculated i.e. with a plate size of 1.0 m x 1.0 m, with cake thickness of 25 cms, $40 \text{ such plates} = 1 \text{ m}^3$ of cake per cycle. In practice the volume of

cake is less than this due to the system of water recovery not allowing 100% complete cake volume. A press cycle occupies some 3 - 5 hours, therefore two cycles may be produced within a normal working day, with the possibility of up to five cycles per day if operated over 24 hours.

Filter Presses are available in a wide range of sizes :-

Plate Size mm.	No. of Plates	Cake Thickness mm.	Volume of Cake per cycle m3
500 x 500	10 - 50	23 - 25	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
630 x 630	20 - 80	2 3 - 25	
800 x 800	40 - 100	28 - 30	
1000 x 1000	60 - 120	33 - 35	
1200 x 1200	40 - 120	33 - 35	
1450 x 1450	40 - 120	38 - 40	

Typical Filter Press basic specification :-

Filter Presses are available with manual operation of the pressure control and manual unloading of the cake - quite satisfactory with small units - or with all operations automatic.

2. <u>Typical Budget Prices</u> were sought from manufacturers capable of handling cake of (i) 0.2 m³/day employing 2 - 4 cycle/day (ii) 1.2 m³/day (iii) 4.0 m³/day

The responses are given below in alphabetical order :-

(a) Supplier Ref. No. 31

(Ъ

	(1)	0.5 m x 0.5 m plates - 11 off 30 mm cake manual	•	US	\$ 7,900
	(11)	0.63 m x 0.63 m plates - 37 off 30 mm ca semi-automatic	ke O	<u>''</u>	\$ 15,200
	(111)	1.0 m x 1.0 m plates - 46 off 32 mm. Fully automatic	0	US	\$ 43,600
)	Suppl	ier Ref. No. 54			
	(i)	0.63 m x 0.63 m plates - 16 off manual	0	US	\$ 8,028
	(ii)	1.0 m x 1.0 m plates - 34 off - auto.	0	US	\$ 27,323
(c) <u>Supp</u>]	lier Ref. 78			
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	(i)	0.5 x 0.5 m plates - 20 off - 32 mm cake manual	<u>us \$</u> 8,424		
	(11)	0.63 x 0.63 m plates - 70 off - 32 mm cake manual <u>US \$ 27,700</u> Auto @	US \$ 36,000		
	(iii)	1.0 x 1.0 m plates - 90 off - 32 mm cake Auto @	US \$ 88,000		
(d) <u>Suppl</u>	ier Ref. 65			
	(i)	0.6 x 0.6 m plates - 16 off - 25 mm cake manual	<u>US \$ 11,606</u>		
	(ii)	1.0 x 1.0 m plates - 24 off - 25 mm cake semi-automatic	US\$ 29,000		
	(111)	1.0 x 1.0 m plates - 57 off - 25 mm cake semi-automatic	US \$ 42,580		
It	ems ii a	nd iii above full automatic operation			
av	ailable	at circa	US \$ 12,000 EXTRA		
(e) <u>Suppl</u>	ier Ref. 86			
	(i)	0.5 x 0.5 m plates - 20 off - 20 mm cake manual	<u>US</u> \$ 11,718		
	(ii)	0.8 x 0.8 m plates - 40 off - 20 mm cake semi-automatic	US \$ 25,307		
	(111)	1.0 x 1.0 m plates - 90 off - 20 mm cake Auto @	US \$ 92,895		
(f) Suppl	ier Ref. 88			
	(i)	0.63 x 0.63 m plates - 15 off - 20 mm cake			
		mamual 0	US\$ 13,011		
	(11)	0.80 x 0.80 m plates - 60 off - 20 mm cake manual	<u>US \$ 37,000</u>		
	(111)	1.2 x 1.2 m plates - 95 off - 20 mm cake Fully automatic	US\$ 96,600		
NOTE:	(1) Th the acco	e output of the above presses may be obtained table given earlier - extrapolating where no rding to the number of plates.	l fron ecessary		
	(2) Th pump smal	e above prices include the necessary high press which account for almost 40% of the cost of ler units, declining to some 20% for the large	essure f the ge units.		
	(3) Al nece has	l references to sizing of filter presses assusting preconditioning with lime and/or ferric been carried out.	umes the salts		

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T BELT PRESSES

Potential Suppliers: Ref. Nos:

5/16/27/36/43/52/61/ 76/94/95/103

1. High Dewatering Capacity

The recent emergence of Belt Presses has widened the choice of sludge dewatering equipment. Belt presses, usually operating two endless sieve bands of synthetic fibre mesh running over a series of rollers which convey, dewater and press the sludge, have low capital and running costs given their outputs. However, even the smallest unit commercially available at this time, 0.4 m belt width, has a nominal capacity of $3 - 7 \text{ m}^3/\text{hr}$, i.e. $72 - 168 \text{ m}^3/\text{day}$ sludge, and as such is suitable for a tannery with a total effluent $500 \text{ m}^3/\text{day}$.

Belt presses require preconditioning and flocculation of the sludges and most units have inbuilt dosing and mixing vats. It is normal for Belt Presses to yield a final sludge of some 28 - 35% D.S.

Typical capacities of Belt Presses are reported :-

Nominal Sludge Capacity Input m ³ /hour
3 - 7
8 - 18
12 - 27
18 - 36

(a) Typical Budget Prices

(i) Supplier Ref. No. 94

Belt Wie	dth 0-4	m	US	\$	39,1	90	Capacity	88	above	
Belt wie	dth 1.0	m	US	Ş	43,8	<u> 388</u>	n	n	n	
Belt wi	dth 1.5	m	US	\$	49,9	950	n	n	11	
Belt wie	dth 2.0	m	US	\$	57,1	162	n	Ħ	n	

(ii) Suppliers Ref. Nos. 43/95

Belt Width	1•0 m	US\$ 63,000	Sludge	Capacity
			2 15	-3 Marine

(iii) Supplier Ref. No. 61.

Belt Width	0•5 m	US \$	80,000	300 - 450 Kg
Solids/hour	Loading rate			

(1V) Supplier No. (. 76	er No	Suppl	(iv)
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Belt Width	0•5 m	US \$	31,740
Belt width	1•2 m	US \$	山.925

Price includes pump, flocculators and washing devices.

S 2 Lower Dewatering Capacity

An interesting new entry to the field of dewatering devices is a new high capacity belt dewatering unit which, while not over sophisticated, is very much cheaper than the above units. It is said to be able to handle from $2 - 10 \text{ m}^3$ /hour slurry input yielding a easily handled final sludge, of some 12 - 18% D.S.

Budget Price	US \$ 1	11,831	Basic
	7 IS \$ 1	14,085	Including flocculator

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U CENTRIFUGES

The dewatering principles of centrifuges are well known. The application of centrifuges to dewatering of tannery sludges has recently expanded and centrifuges are now operating at tannery effluent treatment plants in France, Germany (F.R.) and Japan. Major advantages of centrifuge type decanters are the ease, regularity, and cleanliness of operation. However, whether such fast running plant, up to 3,500 RPM, imposing high demands on its bearings, would be suitable in many developing countries where servicing facilities are poor, may be questioned. However, the employment of such equipment in large tanneries located in Newly Industrialized countries could be envisaged.

Outline specification and budget prices (Suppliers No. 43/95) Centrifugal Sludge Decanters :-

	Small Unit	Medium Unit
Inner Diameter mm Maximum Speed RPM Throughput m ³ /hr Cake Dryness % D.S.*	340 3,500 8 - 15 10 - 35%	530 2,250 20 - 40 10 - 35%
Budget Price US \$	31,690	62,000

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Dependent on type of sludge (Primary/Secondary).

V CHROME RECYCLING UNITS

Potential Suppliers: Ref. Nos: 30/57

A number of suppliers offer package plants for chrome recovery and reuse. The systems are not directly comparable as systems employed may vary in efficiency and ease of control.

Typical offering is (Supplier Ref. No. 30) :-

Screening of used chrome - storage - precipitation vacuum filtration (float to reuse for pickle) - redissolving -All with full automatic control.

Standard Units available 7/10/15/20/30/40/50 m³ chrome float/day. Typical Budget Price for Package Type units

$7 \text{ m}_{2}^{3}/\text{day}$	y chrome	float	US :	95,000
$20 \text{ m}_3/\text{day}$	y 11	Ħ	US .	148,500
$50 \text{ m}^3/\text{dag}$	у "	Ħ	US :	284,000

(Self evidently the amount of chrome available for recovery is dependent on the degree of fixation obtained during tanning).

W LIME RECYCLING UNITS

Potential Suppliers: Ref. Nos: 30/57

The range of techniques available for recycling of lime is large although most package plants offered employ vacuum filtration or UF/RO systems. A typical offering (<u>Supplier Ref. 30</u>) employs vacuum filtration to retain the suspended solids and much of the organic load present in the used lime liquor with the filter. The clarified liquor is subsequently mended with lime and sulphide etc. and recycled for use with savings approaching 50% of chemicals employed.

Typical Budget Prices for such complete plant are:-

$25 \text{ m}_{3}^{3}/ \text{ day I}$	ime Float	US \$	100,000
$35 \text{ m}_3^2/\text{ day}$	n n	US \$	119,555
75 m ³ / day	n n	US \$	210,110

(Alternate capacities available)

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SECTION III B - SUPPLIERS ADDRESSES

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5	ANDRITZ A - 8045 Gras-Andrits Reichsstrasse 66 AUSTRIA	18	DIALI COMPAIR INDUSTRIAL LTD, P O Box 44/Meavell Works/ Renelagh Roed/IP2WICH 1P2 OAR U.K.	31	EDMARDS & JONES LTD. Whittle Road/ MEIR/ STORE-ON-TRENT ST3 7gp
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10	Via Teonghio Li 360Lo ORGIANO (VI) 17ALY. BIRD MACUTHE THETEMATIONAL	24	20125 MILAN <u>ITALY</u> DEL MONTE (AWETO DEL MONTE)	36	UTAH 84110 U.S.A. ESMIL LED Station Road/ST. MHOTS/
	Straatweg 31/ 3603 CV Haarssen P 0 Box 361 3600 Aj Haarssen	~	Via Langhirano 134 L3100 PARMA ITALY	37	Cambs F519 107 U.K. STA (EMORNHARIA DE TRATAMENTOS DE AQUAS LIDA/
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80	PEABODY HOLMES LIMITED Turnbridge/Huddersfield HD1 5RB <u>U.K.</u>	91	U.K. SEAC s.r.l. Via Leone Pancaldo 3/35 50127 FIRENZE	101	TURO ITALIA S.P.A. Viale Zara 58 20124 Milan ITALY
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85	PRINCE MACARONI MANU. CO. (Chem-Tech International) P 0 Box 98/Merrimack & South Union Streets/ LAWRENCE/Massachusetts 01843 Area Code 517 685-4301 U.S.A.	96	B. S. SMOGLESS S.p.A. Via Mascheroni 29 20145 MILAN ITALY	105	WOODS OF COLCHESTER LTD. Tufnell Way COLCHESTER COL 5AR U.K.







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Fig. N (111) PERIPHERAL ENTRY SEDIMENTOR Scum Rotaining Curtain Supernatant Sludge Discharge



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REFERENCES

- 1 "Environmental Considerations in the Leather Producing Industry" Draft Project Final Report UNIDO/ITD. 337 9 June 1975
- 2 "Eleventh Meeting of the I.U.L.T.C.S. Tannery Wastes Commission" via J. Soc. Leather Technol. Chem. 1979. (63) 114-125
- 3 Waste Management Paper No. 17 "Wastes from Tanning, Leather Dressing and Fellmongering". Department of the Environment, LONDON 1978.
- Bartlett + James J. Environmental Quality 1979. 8. (1) 31., via
 Meeting of the I.U.L.T.C.S. Tannery Wastes Commission. J. Soc.
 Leather Technol. Chem. 1981. (65) 91.
- 5 Meeting of the I.U.L.T.C.S. Tannery Wastes Commission. J.Soc. Leather Technol. Chem. 1981. (65) 91.
- 6 Muralidhara H.S. and Maggin B. "Recovery of Energy and Chrome from Leather Waste". The Leather Manufacturer. September 1979. P.30
- 7 Jones B.H. "Incineration and the Environment". The Leather Manufacturer June 1980 P. 31
- 8 Muralidhara H.S. "Letter to the Editor" The Leather Manufacturer August 1980 P. 37
- 9 Jones B.H. "Low Temperature Alkaline Incineration of Leather Shavings and Tannery Sludges". The Leather Manufacturer December 1980 P. 29
- 10 "Leather Tanning and Finishing Point Source Category". EPA 440/1-74-016-a Washington March 1974
- 11 Aloy, Folachier and Vulliermet "Pollution and Tannery". Centre Technique du Cuir. Lyons, France May 1976
- 12 Calculated by the UNIDO Consultant from data quoted by Fendrup at reference 2 above.
- 13 Calculated by the UNIDO Consultant from data quoted by Gorecki at reference 2 above.

- 14 Hervey R.K. Bot. Gaz. 111 (1) 1 (1949)
- 15 Southgate B.A. "Treatment and Disposal of Industrial Waste Waters". Department of Scientific and Industrial Research H.M. Stationery Office, London 1948
 - 16 van Vlimmerent P.J. "Tannery Effluent". I.A. Wilson Memorial Lecture 1972. J.Am. Leather Chem. Ass. 1972, 67, 388-406
 - 17 Tannery Effluent. Report to the members of the Effluent Commission of the IULCS. Journal Soc. Leather Trades Chem. 1972. (56) 40-71
 - 18 Folachier: A; Reynaud P: "Reduction des volumes d'eau utilisés en fabrication (rincages et lavages) Technicuir 1973, 7, No. 2 3-9
 - 19 Folachier A: "Les "points chauds" de la pollution en tannerie-megisserie". Technicuir 1974, 8 (No.7) 20-3 (1974)
 - 20 Slabbert N.P: Recycling in the Tanning Industry. L.I.R.I. J. Soc. Leather Technol. Chem. 1980 (64) 89.
 - 21 Komanowsky M; Senske G.E. "Reduction of Tannery Waste Volume Through Countercurrent Reuse of Process Streams". J.A. Leather Chem. Ass. 1982. Page 206
 - 22 Simoncini A; de Simone G: "Depuration en Continu des Eaux de Rivière, tannage et teinture, à l'Exterieur du Foulon" XVII Congress I.U.L.T.C.S. Buenos Aires 1981.
 - 23 Folachier A: "Recyclage direct des Bains de Pelange et de tannage au Chrome en Fabrication". XIV Congress I.U.L.T.C.S. Barcelona 1975
 - 24 van Vlimmeren P.J.; Langerwerf J.S.A.; van Meer A.J.J; Pelckmans H.H.A.: "New Developments in the Lime-Sulphide Unhairing Process to Improve the Quality of Tannery Waste Water". XIV Congress I.U.L.T.C.S. Barcelona 1975

25 Ludvik J: Ref. 5 ibid.

-153-

- 26 Frendrup W. Ref 5 ibid
- 27 Frendrup W. Ref 2 ibid
- 28 Cranston R.W; Davis M.H.; Scroggie J.G.: "Improvements in The Unhairing Process". XVII Congress I.U.L.T.C.S. Buenos Aires 1981

29 Frendrup W. "The Influence of Unhairing Methods upon the Amount and Degree of Water Pollution from a Tannery: A Survey of the Literature 1967 - 73". J.Soc. Leather Technol. Chem. 1974 (58) 9.

- 30 Prentiss W.C.: "Chemical Routes to a Low Sulfide Beamhouse". The Leather Manufacturer Spetember 1981 Page 21
- 31 Sukach D.S.: "Use of an Enzyme Soak for Rapid Liming in Normal and Low Sulfide Systems". The Leather Manufacturer September 1981 Page 25.
- 32 Fritz H: "Sulfide-free Unhairing Systems Can Avoid Pollution Problems". The Leather Manufacturer October 1979 P. 32.
- 33 Gaughhofer J: via "Tenth Meeting I.U.L.T.C.S. Tannery Wastes Commission 1977" J.Soc. Leather Technol. Chem. 1979 (63) 6.
- 34 Simoncini A; Del Pezzo; Manzo: Cuoio. Pelli. Mat. Coneianti 1972, (48) 337
- 35 Frendrup W: via I.U.L.C.S. Effluent Commission. J.Soc. Leather Technol. Chem. 1973 (57) 63
- 36 Money C.A.; Adminis U: "Recycling of Lime-Sulphide Unhairing Liquors". J.Soc. Leather Technol. Chem. 1974 (58) 35.
- 37 Schubert B; Pauckner: "Recycling Unhairing Liquor to Reduce Effluent Pollution". Gerbereiwiss Prax. 1977, 29 (24) 218 - 230. via J. Soc. Leather Technol. Chem. 1979 (63) 40.
- 38 Luck W: "Chrome Tanning Processes with Particularly Good Exhaustion". The Journal of the American Leather Chemists Ass. 1980 (75) 10 378

-154-

- 39 Covington A.D: "Studies in Chrome Utilization in U. K. Tanneries" Part I J. Soc. Leather Technol. Chem. 1981 (65) 1
- 40 Davis M.H. Scroggie J.G. : "Investigations of Commercial Chrome Tanning Systems" Part I "Separation of the Complexes present by Gel Filtration and the Effects of Aging and Basification". J. Soc. Leather Technol. Chem. 1973 (57) 13
- 41 Ibid Part II "The Rate of Uptake by Hide of the Different Chrome Complexes from Solution!" J. Soc. Leather Technol. Chem. 1973 (57) 35
- 42 Ibid Part III "Recycling of Used Chrome Liquors". J. Soc. Leather Technol. Chem. 1973 (57) 53
- 43 Ibid Part IV "Recycling of Chrome Liquors and Their Use as a Basis for Pickling". J. Soc. Leather Technol. Chem. 1973 (57) 81
- Liµ Ibid Part V "Recycling of Chrome Liquors in Commercial Practics" J. Soc. Leather Technol. Chem. 1973 (57) 173
- 45 Burns J.E.; Colquitt D.E.; Davis M.H; Scroggie J.G. :"Investigation of Commercial Chrome-Tanning Systems. Part VI Full-scale Trials of Chrome Liquor Recycling and the Importance of Salt Concentration". J. Soc. Leather Technol. Chem. 1976 (60) 106
- 46 Arnoldi H.W.; Covington A D: "Studies in Chrome Utilization in U.K. Tanneries" Part II. J. Soc. Leather Technol. Chem. 1981 (65) 5
- 47 Sharp B. via "Solutions to Pollution discussed by A.L.C.A" The Leather Manufacturer 1980 (7) Page 20
- 48 Constantin J.M.; Stockman G.B.: "Leather Tannery Waste Management Through Process Change, Reuse and Pretreatment". Industrial Environmental Research Laboratory U.S. Environmental Protection Agency EPA-600/2-77-034 January 1977
- 49 Langerwerf J.S.A.; de Wijs J.C.; Pelckmans H.H.X; Koopman R.C.: "Precipitation and Reuse of Trivelent Chromium". IIV Congress I.U.L.T.C.S. Barcelona 1975 Page 27
- 50 Langerweif J.S.A.; Pelckmans H.H.A; "Chromium Containing Wastes of the Leather Industry". XVII Congress I.U.L.T.C.S. Buenos Aires 1981.

"Unique Chrome Recycling System at Wolverine Worldwide Reduces 51 Discharge Level and Chemical Costs" - The Leather Manufacturer August 1979 Page 38 "The Liritan "No Effluent" Rapid Pit Tannage 52 Shuttleworth S.G: J. Soc. Leather Trades Chem. 1963 (47) Sole Leather Process". 143 "An Efficient and Economical Scowcroft F: 53 Atkinson J.H: Tannage of Light Leathers" Modern Methods of Tannage TEPF Zurich "The Removal of Sulphide from 54 Bailey A.D: Humphreys F.E: J. Soc. Leather Trades Chem. Limeyward Wastes by Aeration". 1967, (51) 154. "Some Aspects of Tannery Effluent Control" J. Am 55 De S: Leather Chem. Ass. 1973 (68) 8. 316 Minutes of the 8th Meeting of the I.U.L.T.C.S. Tannery Wastes 56 Commission May 1975 via J. Soc. Leather Technol. Chem. 1976 (60; 95 "The Treatment of Beamhouse and Fellmongery 57 Stevens W: Annual Conference S.L.T.C. Leicester. October 1982 Effluent". Twelth Meeting of the I.U.L.T.C.S. Tannery Wastes Commission 1979 58 J. Soc. Leather Technol. Chem. 1980 (64) 109 "Chemical Treatment Solves Tannery Waste Problems" 59 Giles M: Industrial Wastes. March/April 1980 Arnoldi H.W: Corning D.R: Sykes R.L: "The Application of 60 Flotation Techniques to the Treatment of Tannery Waste Waters" J. Soc. Leather Technol. Chem. 1980 (64) 69 "New Treatment for Effluent" - "LEATHER" - International Journal 61 of the Industry September 1981 page 188

39	Covington A.D: "Studies in Chrome Utilization in U. K. Tanneries" Part I J. Soc. Leather Technol. Chem. 1981 (65) 1
Ц О	Davis M.H. Scroggie J.G. : "Investigations of Commercial Chrome Tanning Systems" Part I "Separation of the Complexes present by Gel Filtration and the Effects of Aging and Basification". J. Soc. Leather Technol. Chem. 1973 (57) 13
41	Ibid Part II "The Rate of Uptake by Hide of the Different Chrome Complexes from Solution" J. Soc. Leather Technol. Chem. 1973 (57) 35
42	Ibid Part III "Recycling of Used Chrome Liquors". J. Soc. Leather Technol. Chem. 1973 (57) 53
43	Ibid Part IV "Recycling of Chrome Liquors and Their Use as a Basis for Pickling". J. Soc. Leather Technol. Chem. 1973 (57) 81
յիլ	Ibid Part V "Recycling of Chrome Liquors in Commercial Practice" J. Soc. Leather Technol. Chem. 1973 (57) 173
45	Burns J.E.; Colquitt D.E.; Davis M.H; Scroggie J.G. :"Investigation of Commercial Chrome-Tanning Systems. Part VI Full-scale Trials of Chrome Liquor Recycling and the Importance of Salt Concentration". J. Soc. Leather Technol. Chem. 1976 (60) 106
Ц6	Arnoldi H.W.; Covington A D: "Studies in Chrome Utilization in U.K. Tanneries" Part II. J. Soc. Leather Technol. Chem. 1981 (65) 5
47	Sharp B. via "Solutions to Pollution discussed by A.L.C.A" The Leather Manufacturer 1980 (7) Page 20
<u>ц</u> 8	Constantin J.M.; Stockman G.B.: "Leather Tannery Waste Management Through Process Change, Reuse and Pretreatment". Industrial Environmental Research Laboratory U.S. Environmental Protection Agency EPA-600/2-77-034 January 1977
49	Langerwerf J.S.A.; de Wijs J.C.; Pelckmans H.H.K; Koopman R.C.: "Precipitation and Reuse of Trivalent Chromium". XIV Congress I.U.L.T.C.S. Barcelona 1975 Page 27

50 Langerweff J.S.A.; Pelckmans H.H.A; "Chromium Containing Wastes of the Leather Industry". XVII Congress I.U.L.T.C.S. Buenos Aires 1981.

-155-

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- 51 "Unique Chrome Recycling System at Wolverine Worldwide Reduces Discharge Level and Chemical Costs" - The Leather Manufacturer August 1979 Page 38
- 52 Shuttleworth S.G: "The Liritan "No Effluent" Rapid Pit Tannage Sole Leather Process". J. Soc. Leather Trades Chem. 1963 (47) 143
- 53 Atkinson J.H: Scowcroft F: "An Efficient and Economical Tannage of Light Leathers" Modern Methods of Tannage TEPF Zurich
- 54 Bailey A.D: Humphreys F.E: "The Removal of Sulphide from Limeyward Wastes by Aeration". J. Soc. Leather Trades Chem. 1967, (51) 154.
- 55 De S: "Some Aspects of Tannery Effluent Control" J. Am Leather Chem. Ass. 1973 (68) 8. 316
- 56 Minutes of the 8th Meeting of the I.U.L.T.C.S. Tannery Wastes Commission May 1975 via J. Soc. Leather Technol. Chem. 1976 (60) 95
- 57 Stevens W: "The Treatment of Beamhouse and Fellmongery Effluent". Annual Conference S.L.T.C. Leicester. October 1982
- 58 Twelth Meeting of the I.U.L.T.C.S. Tannery Wastes Commission 1979 J. Soc. Leather Technol. Chem. 1980 (64) 109
- 59 Giles M: "Chemical Treatment Solves Tannery Waste Problems" Industrial Wastes. March/April 1980
- 60 Arnoldi H.W: Corning D.R: Sykes R.L: "The Application of Flotation Techniques to the Treatment of Tannery Waste Waters" J. Soc. Leather Technol. Chem. 1980 (64) 69
- 61 "New Treatment for Effluent" "LEATHER" International Journal of the Industry September 1981 page 188

62	Poole B.M: "Enhanced Clarification of Tannery Wastewater" J. Am. Leather Chem. Ass. 1982 (77)
63	van Vlimmeren P.J: van Meer A.J.J: "Recent Investigations into the Disposal of Tannery Waste Waters" The Leather Manufacturer 1974 Page 24
64	Berk W.J: "Treat Your Tannery Waste to an Oxidation Ditch" J. Am. Leather Chem. Ass. 1982 (77) 38
65	Bailey D.A: Plowright D.G: "Oxidation Ditches for Treating Tannery Effluent" "LEATHER" - International Journal of the Industry July 1978 Page 35
66	M Aloy, C.T.C. Lyons - Personal communication.
67	Trentelman C.C.M: Epskamp R.J.C: "System Choice for the Treatment of Wastewater": Conference Paper Amsterday Oct. 1982.

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