EPA 440/1-73/015

DEVELOPMENT DOCUMENT FOR PROPOSED EFFLUENT LIMITATIONS GUIDELINES AND NEW SOURCE PERFORMANCE STANDARDS FOR THE

LEATHER TANNING AND FINISHING

POINT SOURCE CATEGORY

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

NOVEMBER 1973

DEVELOPMENT DOCUMENT

for

PROPOSED EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

LEATHER TANNING AND FINISHING POINT SOURCE CATEGORY

Russell Train
Administrator

Robert L. Sansom
Assistant Administrator for Air & Water Programs

Allen Cywin
Director, Effluent Guidelines Division

James D. Gallup
Project Officer

November 1973

Effluent Guidelines Division
Office of Air and Water Programs
U. S. Environmental Protection Agency
Washington, D. C. 20460

ABSTRACT

This document presents the findings of an extensive study of the leather tanning and finishing industry for the purpose of developing effluent limitations guidelines, standards of performance, and pretreatment standards for the industry, to implement Sections 304, 306, and 307 of the Federal Water Pollution Control Act, as amended.

Effluent limitations guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable; these levels of treatment must be achieved by existing sources by July 1, 1977, and July 1, 1983, respectively. The standards of performance for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology.

The proposed regulations for July 1, 1977, and for new source performance standards are based on preliminary screening, equalization and primary sedimentation, secondary biological treatment and chrome recycle.

The recommended technology for July 1, 1983, is preliminary screening, equalization and primary sedimentation, secondary biological treatment and chrome recycle plus sulfide oxidation, nitrification and denitrification and mixed-media filtration.

Supportive data and rationale for development of the proposed effluent limitations guidelines and standards of performance are contained in this report.

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SECTION I

CONCLUSIONS

For purposes of establishing effluent limitations guidelines and standards of performance, the leather tanning and finishing industry has been divided into six major subcategories. These subcategories have been derived principally by similarities in process and waste loads. Such factors as age and size of plant, climate, and waste control technologies favor segmentation of the industry into these six subcategories. The following tabulation is a capsule summary of these subcategories:

INDUSTRY SUBCATEGORIES

	Primary Processes		
Subcategory	Beamhouse	Tanning	Leather Finishing
1	Pulp hair	Chrome	Yes
2	Save hair	Chrome	Yes
3	Save hair	Vegetable	Yes
4	Hair previously removed	Previously tanned	Yes
5	Hair previously removed or retained	Chrome	Yes
6	Pulp or save hair	Chrome or no tanning	No

Currently, waste from about 60 percent of the tanneries (and approximately 60 percent of the production) is discharged to municipal sewer systems, while the remainder is discharged directly to surface waters.

Compared with other industries, waste treatment facilities for those plants in the leather tanning and finishing industry discharging directly to rivers or streams are severely lacking. There are no exemplary waste treatment plants handling only tannery waste.

It is concluded that the technology is available to effect considerable improvement in waste discharges with major removal of BOD_5 and suspended solids by July 1, 1977. The estimated capital cost of achieving effluent limitations (the best practicable control technology currently available) by tanneries discharging to receiving waters is $28 million (August, 1971, price levels). Total annual costs (including depreciation, interest, operation, and maintenance) for pollution control will increase finished product costs from about 1.1 to 3.5

percent (August, 1971, prices) depending on industrial subcategory. For only one subcategory is the increase in excess of 2.6 percent.

It is further concluded that by July 1, 1983, implementation of treatment facilities to effect further removal of BOD and SS as well as major removal of sulfide and nitrogen (the best available control technology economically achievable) will be required for facilities discharging directly to surface waters. Total capital investment for achieving 1983 effluent limitations is estimated at about $42.5 million (August, 1971, prices). This represents an additional $14.5 million investment over BPCTCA. Total annual costs for the best available control technology economically achievable will increase finished product prices from about 0.5 to 2.6 percent (August, 1971,prices) for differing subcategories. The overall cost of both best practicable and best available control technology is estimated to increase final product costs from 1.6 to 6.1 percent for various subcategories and only one subcategory is in excess of 3.8 percent.

Some economies may be achieved during implementation of the best available control technology economically achievable waste treatment facilities if the industry can find a substitute for ammonia compounds used in the bate process. However, organic nitrogen from processing hides will still require some degree of nitrification-denitrification facilities.

Standards of performance for new sources are equivalent to the best practicable control technology currently available requirements.

Complete reuse of treated effluent cannot be achieved without removal of dissolved solids. Methods for removing dissolved solids and subsequent disposing of the concentrated brines are not sufficiently defined technically or economically to enable implementation without a great degree of risk. In addition, a further complicating factor is imposed if dissolved solids removal becomes a requirement for those tanneries providing only pretreatment for discharge to a municipal system. Since an extremely good quality water is necessary as an influent to processes capable of dissolved solids removal, all tanneries, regardless of discharge point, would require installation of major biological treatment facilities in addition to that required for dissolved solids removal.

SECTION II

RECOMMENDATIONS

Presented herein are the recommended effluent limitations guidelines for the leather tanning and finishing industry. The proposed basic levels of waste constituents in the following tabulations are recommended to be the average values based on production data and analyses of 24-hour composite samples collected during any 30-day period. However, the pH should never exceed values shown as measured by grab or composite samples. Due to process upsets, emergencies such as a power failure and other such occurrences, there are times when these average values may be exceeded. The daily maximum allowable level proposed for all parameters except pH is two times the basic values presented here. Such a maximum allowable level would be checked by composite samples collected at any time.

Application of the best practicable control technology currently available, as shown in Table 1 results in the effluent limitations guidelines to be met by July 1, 1977, for tanneries discharging directly to surface waters.

Application of the best available control technology economically achievable results in the effluent limitations guidelines shown in Table 2 for tanneries discharging directly to surface waters. These limitations are to be achieved by July 1, 1983.

Effluent limitations guidelines for new tanneries yet to be built (New source performance standards) are the same as for the best practicable control technology currently available.

The requirement to remove dissolved solids by 1983 is not recommended. The technology for widespread removal of dissolved salts and disposal of concentrated brines is not well defined. Extensive research efforts should be made by the industry to find a substitute for salt used in hide curing, which is a major contributor of the dissolved solids.

The technologies to which the above limitations and standards are based assume extensive water and chemical conservation within the industry and properly designed and operated waste treatment facilities.

TABLE 1

BEST PRACTICABLE EFFLUENT LIMITATIONS
(July 1, 1977)

PARAMETER(1)	SUBCATEGORY kg/1000 kg hide (lb/1000 lb hide)					
	1	2	3	4	5	6
BOD_5	2.7	3.2	2.5	1.0	3.2	1.4
TOTAL CHROMIUM	0.05	0.06	0.05	0.02	0.06	0.03
OIL & GREASE	0.53	0.63	0.50	0.24	0.63	0.34
SS	3.0	3.5	2.8	1.1	3.5	1.5

(1) For all subcategories pH should range between 6.0 and 9.0 at any time

For all subcategories Most Probable Number (MPN) of Fecal Coliforms should not exceed 400 counts per 100 ml

TABLE 2

BEST AVAILABLE EFFLUENT LIMITATIONS
(July 1, 1983)

PARAMETER(1)	SUBCATEGORY kg/1000 kg hide (lb/1000 lb hide)					
	1	2	3	4	5	6
BOD5	1.35	1.60	1.25	0.50	1.60	0.70
TOTAL CHROMIUM	0.05	0.06	0.05	0.02	0.06	0.03
OIL & GREASE	0.53	0.63	0.50	0.24	0.63	0.34
SULFIDE	0.005	0.006	0.005	0.002	0.006	0.003
SS	1.5	1.8	1.4	0.6	1.8	0.8
TKN	0.27	0.32	0.25	0.10	0.31	0.14

(1) For all subcategories pH should range between 6.0 and 9.0 at any time

For all subcategories Most Probable Number (MPN) of Fecal Coliforms should not exceed 400 counts per 100 ml

SECTION III

INTRODUCTION

Scope

The 1972 Amendments to the Federal Water Pollution Control Act require the U. S. Environmental Protection Agency to establish effluent limitations which may be achieved by point discharge sources into navigable waters. For existing waste sources, the Act requires application of the best practicable control technology currently available by July 1,1977, and application of the best available control technology economically achievable by July 1, 1983. For new waste sources, the best available demonstrated control technology must be applied.

The broad objectives of this study are to establish the control and treatment technology available and to present suggested effluent limitation guidelines and standards of performance applicable to the leather tanning and finishing industry. The principal elements of the study are as follows:

1. Establish the various subcategories within the leather tanning and finishing industry subject to effluent limitations and standards of performance.

2. Characterize wastes from each major subcategory of the industry by assessing flows and constituents in the waste water.

3. Establish existing and potential control and treatment technologies applicable to each subcategory of the industry. Such technology includes in-plant controls, end-of-process control and treatment, and pretreatment prior to discharge to a publicly-owned waste water system.

4. Outline the best practicable control technology currently available and the best available treatment technology economically achievable for establishing effluent limitation guidelines.

5. Prepare a report summarizing control and treatment technology, together with suggested effluent limitations guidelines and appropriate cost information.

Previous Study

A principal source of information for this investigation is the "Industrial Waste Study of the Leather Tanning and Finishing Industry" conducted for the Water Quality Office, U. S. Environmental Protection Agency, by Stanley Consultants (October, 1971). Relevant data from that study are included herein.

Industry Trends

The number of tanneries in the U. S. has steadily decreased from around 7,500 operating in 1865 to approximately 1,000 by the year 1900 (1). The number has continued to decrease from the turn of the century to about 200 to 210 tanneries (wet process) in operation at the present time. Another 225 to 260 firms are engaged in finishing operations (essentially dry process) on leather tanned at some other location.

Tanneries are principally clustered in the New England and Mid-Atlantic states, Chicago-Milwaukee area, and Gloversville-Johnstown area in New York. Others are scattered throughout the U. S.

Since about 1960, several significant developments have taken place in the domestic tanning industry. Most noteworthy is the increased export of cattlehides to countries for production of leather. In 1972, hides from over 47 percent of the 36.5 million cattle slaughtered in the U. S. went to foreign tanners (2). Since 1960, export of hides has more than doubled, while domestic tanning has reduced slightly. The increased number of export cattlehides has mainly gone to Japan. Lower labor costs seem to enable foreign countries to compete in the U. S. leather and leather products industry; hence, the greater demand for hides.

Exporting hides for tanning has also had a pronounced effect on the finished product market. For example, in 1960, imported shoes accounted for about 4.3 percent of the U. S. market, contrasted to over 36 percent of the 1972 market (2). With the increased import of shoes, domestic tannage has been used proportionately more for clothing and other uses.

Other changes in the leather industry include increasing use of leather substitutes, such as plastic, which have absorbed a larger portion of the total market. Experimentation with other synthetic products may yield further competitive materials.

From an economic standpoint, the domestic leather tanning and finishing industry has recently felt a squeeze from both ends--raw material and finished product. Greater foreign demand for cattlehides has resulted in part from a change in a restrictive hide export policy by other hide producing nations. This has recently caused the price of raw cattlehides to increase greatly. Heavy native steer hides have ranged in price from 8.3 to 20.3 cents per pound in the period 1960-71. Average price in 1971 was 14.4 cents per pound. In 1972 prices increased to 42.4 cents in August, with an average for the year of 29.7 cents per pound. These raw product prices have now fallen to about twice those in 1971. In addition, competition from foreign countries such as Japan, Italy, and Spain in the finished leather products market has reduced the potential revenue from domestic leather firms.

Cattlehides constitute the bulk of the tanning done in the U. S., representing about 90 percent of the estimated pounds of hides tanned.

Sheep and lamb represent about the next largest volume. Pigskin production is estimated to be the third largest production volume in the U. S. Since 1960, domestic tanning of cattlehides, sheepskins, and lambskins has trended slightly downward.

Other types of skins or hides processed in the U. S. include goat, kid, hairsheep, and horse. All of these tanning volumes have fallen significantly since 1960. Various other skins tanned in the U. S. on a very limited basis include deer, elk, moose, antelope, and rabbit, as well as rare skins such as alligator, crocodile, seal, shark, and kangaroo.

SECTION IV

INDUSTRY CATEGORIZATION

Standard Manufacturing Processes

Tanning is the process of converting animal skin into leather. The skin is divided into three layers: flesh, derma or corium, and epidermis. The epidermal and corium layers constitute the leather-making portion of the skins or hides, and consist mainly of the protein collagen after undesirable proteins are removed. Tanning is essentially the reaction of collagen fibers with tannin, chromium, alum, or other tanning agent with the resulting formation of leather.

A major factor affecting waste production in the leather tanning and finishing industry is the type of manufacturing process used to convert the various types of animal skins to the tanned and finished leather. This variance is recognized in the classification system used to describe the industry.

The process of tanning originally developed as an art many centuries ago, but has in recent times been modified by application of scientific principles. As in any industry, the approach to production of a suitable leather by the average tannery relies a great deal on past experience. In a typical process, such as unhairing, the concentration of lime and sharpeners (such as sodium sulfide and sodium sulfhydrate), temperature, and processing time are interrelated. As in most chemical reactions, chemical concentrations and/or temperature may be increased to decrease the processing period. Tanners vary process conditions to control the quality of the finished product. Therefore, there is a significant amount of variance in processing techniques, even between two tanners producing the same finished product, to satisfy individual product needs.

In this study, a manufacturing process is defined as a single step in the complete manufacturing operation where alternative steps may result in significantly different waste characteristics. A process can consist of one or a series of sub-processes. In any defined process, sub-processes would remain the same. The industry can best be described and analyzed on this manufacturing process concept basis. This allows for the variance of processes used among plants. With this approach, waste loads and effluent requirements can be more readily described.

For purposes of characterizing waste loads, there are the following standard applicable processes: beamhouse; tanhouse; retan, color, and fatliquor; and finishing. Chemicals such as lime, sodium sulfide, sodium sulfhydrate, basic chromium sulfate, vegetable compounds, mineral acids, and sodium chloride are employed with the various processes.

The discussion and description of manufacturing processes which follow are based upon the three major hide or skin types produced in the U. S., cattlehides, sheepskins, and pigskins. The processes and sub-processes discussed herein represent an inventory of those most typical of the entire industry. Process descriptions which follow have been kept brief, since more detailed information is readily available from the literature (3) (4).

Cattlehide Tannery Processes

There are four processes in a typical cattlehide tannery which contribute waste loads:

1. Beamhouse.

2. Tanhcuse.

3. Retan, color, and fatliquor.

4. Finishing.

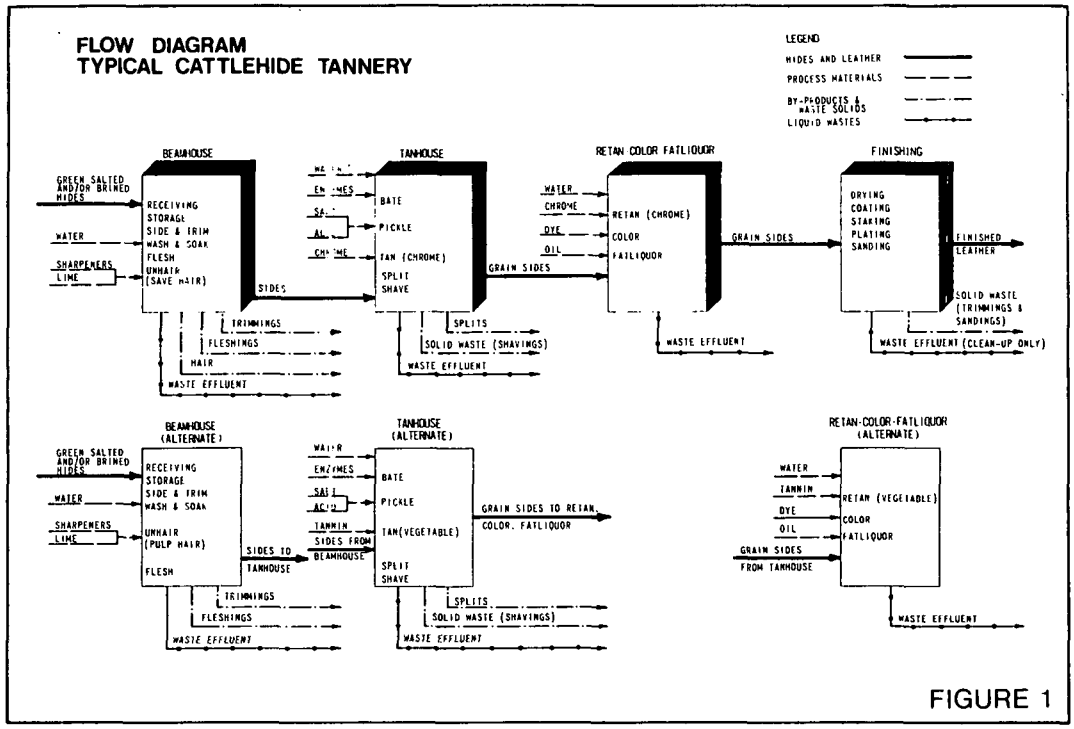

FLOW DIAGRAM
TYPICAL CATTLEHIDE TANNERY
LEGEND
HIDES AND LEATHER
PROCESS MATERIALS
BY-PRODUCTS & WASTE SOLIDS
LIQUID WASTES
BEAMHOUSE
GREEN SALTED AND/OR BRINED HIDES
WATER
SHARPENERS
LIME
RECEIVING
STORAGE
SIDE & TRIM
WASH & SOAK
FLESH
UNHAIR (SAVE HAIR)
SIDES
TRIMMINGS
FLESHINGS
HAIR
WASTE EFFLUENT
TANHOUSE
BATE
PICKLE
TAN (CHROME)
SPLIT
SHAVE
SPLITS
SOLID WASTE (SHAVINGS)
WASTE EFFLUENT
GRAIN SIDES
RETAN COLOR FATLIQUOR
WATER
CHROME
DYE
OIL
RETAN (CHROME)
COLOR
FATLIQUOR
WASTE EFFLUENT
GRAIN SIDES
FINISHING
DRYING
COATING
STAKING
PLATING
SANDING
FINISHED LEATHER
SOLID WASTE (TRIMMINGS & SANDINGS)
WASTE EFFLUENT (CLEAN-UP ONLY)
BEAMHOUSE (ALTERNATE)
GREEN SALTED AND/OR BRINED HIDES
WATER
SHARPENERS
LIME
RECEIVING
STORAGE
SIDE & TRIM
WASH & SOAK
UNHAIR (PULP HAIR)
FLESH
SIDES TO TANHOUSE
TRIMMINGS
FLESHINGS
WASTE EFFLUENT
TANHOUSE (ALTERNATE)
WATER
ENZYMES
TANNIN
SIDES FROM BEAMHOUSE
BATE
PICKLE
TAN(VEGETABLE)
SPLIT
SHAVE
GRAIN SIDES TO RETAN. COLOR. FATLIQUOR
SPLITS
SOLID WASTE (SHAVINGS)
WASTE EFFLUENT
RETAN-COLOR-FATLIQUOR (ALTERNATE)
WATER
TANNIN
DYE
OIL
GRAIN SIDES FROM TANHOUSE
RETAN (VEGETABLE)
COLOR
FATLIQUOR
WASTE EFFLUENT

FIGURE 1

These processes are shown schematically on Figure 1. There are alternate processes for each of the first three basic processes which produce significantly different waste characteristics. Sub-processes and the operations which take place within each process are described as follows:

BEAMHOUSE PROCESS:

1. Receiving - Nearly all cattlehides received at tanneries are either cured green salted or brined hides, with brined hides predominating. In a few isolated cases where transit time is short, green hides without prior curing have been sent directly from a packer to a tannery and processed.

   Green hides, after trimming and grading, are cured at the packing house by spreading the hides flesh side up and covering with salt. Another layer of hides is placed over the salted hides, again flesh side up, and covered with salt. This process continues until a pack of hides about 5 to 6 feet high results. A heavy layer of salt is placed over the top layer of hides. The natural liquid of the hides dissolve a portion of the salt to form a brine. In this process, salt is absorbed and by diffusion and osmosis cause a reduction of the moisture content in the hide. After 10 to 30 days from the date the pack is closed, the hides are considered adequately cured. Each hide then has the excess salt shaken off, is folded individually, and shipped in packs, either to tanneries or to warehouses for storage. The size of the pack depends on a number of variables, such as size of the packing house, size of shipments, and the method of shipment.

   Brined hides are prepared at the packing house or at a separate hide processing facility by agitating fresh hides in a saturated brine solution until the salt has replaced the desired amount of moisture within the hide. In this process, hides are also cleaned by removal of manure and other attached foreign matter. Hides are then removed, drained, and bundled in a manner similar to that used for green salted hides. Hides may be fleshed before or after brining. "Safety salt" is usually sprinkled on each hide before shipment. The brining process takes two to three days, which makes it attractive to the packer or hide curing establishment, since there is no need to hold a large inventory of hides. The brining process is preferred by most tanners since it tends to produce cleaner hides. Increased use of brined hides in recent years demonstrates these preferences by both packer and tanner.

2. Storage - Hides are normally stored at the tannery in the pack as received. No special storage conditions are maintained in

most tanneries other than that required to keep hides at the moisture content as received.

3. Siding and Trimming - The usual first step in the processing of hides from storage at the tannery is to open a folded hide and trim it. The hides then may be cut in half along the backbone, which is referred to as halving or siding. Sometimes hides are halved after unhairing or tanning.

   Sides are usually palletized for transporting to the next step in the process. Trimmings are collected for shipment to glue or other by-product manufacturers.

4. Washing and Soaking - Sides (or in some cases whole hides) from the siding and trimming operation are placed in vats (with or without paddles), drums, or hide processors (concrete mixers with special linings) for washing and soaking to restore moisture. Water usage is generally less with hide processors, although some tannery people have expressed the opinion that equivalent reduction in water use can be achieved with drums.

   In this process dirt, salt, blood, manure, and non-fibrous proteins are removed from the hides. There is considerable variation in the quantity of such waste material, depending on the time of year and the source of the hides.

   Depending on the type of leather produced, additional washes (rinses) may also occur at several other points in the tanning process, including after liming and dehairing, after bating, after tanning, and prior to and following coloring.

5. Fleshing - Fleshing is the removal of attached adipose fatty tissue and meat which have been left on the hide at the packing house. It is done on a fleshing machine, in which the hide is carried through rolls and across rotating spiral blades which remove the flesh from the hide. Cold water is necessary to keep the fat congealed, but the fat represents an additional waste disposal load.

   Most hides are fleshed at the packing house or at a separate hide processing facility, particularly in the case of brined hides. When flesh is removed prior to liming it is referred to as green fleshing; when it is performed after liming it is referred to as lime fleshing. In any case, fleshings are normally recovered and sold to plants for rendering or conversion to glue. If fleshings are properly handled, there is very little liquid or solid waste contribution from this operation.

6. Unhairing - Hair is removed by chemical loosening followed by either machine pulling or chemically dissolving the hair. Machine removal is practiced where it is desired to recover the hair. The dissolving process is referred to as "pulping" or "burning."

   For either type of unhairing, the hides are placed in vats (with or without paddles), drums, or hide processors with a lime slurry to which sharpeners such as sodium sulfide and sodium sulfhydrate added. When the hair is to be saved, the strength of the solution and the time in contact with the hide is limited to that necessary to loosen the hair sufficiently for mechanical pulling. If the hair is to be pulped, stronger solutions and/or longer time cycles are used and the hair may be totally dissolved.

   Sometimes hides are relimed to make the hide swell for easier splitting. In a save hair operation, flesh and hair removal is sometimes followed by a "scudding" step to ensure removal of hair roots and fine hairs.

   The liming and unhairing process is one of the principal contributors to the waste effluent. In a save hair operation with good recovery of hair, the contribution to the effluent is substantially lower than in the pulp hair operation.

TANHOUSE PROCESS:

1. Bating - Bating is the first step in preparing the stock for the tanning process. It may be done in either vats (with or without paddles), drums, or hide processors. The hides are placed in the processing equipment which contains a solution of ammonium salts and enzymes. The purpose of this operation is to:

   a. De-lime skins.

   b. Reduce swelling.

   c. Peptize fibers.

   d. Remove protein degradation products.

2. Pickling - The pickling sub-process follows the bating step and is normally done in the same equipment. A brine and acid solution is used to bring the hides to an acid condition in preparation for subsequent tanning sub-process. In addition to conditioning the hide for receiving the tanning agent, it prevents precipitation of chromium salts.

Pickling is always done before the chrome tanning process and may be done before vegetable tanning.

3. Tanning - Nearly all cattlehides in this country are either chrome or vegetable tanned; very little is tanned with alum or other tanning materials.

   Vegetable tanning is the older process, and is performed in a solution containing plant extracts such as vegetable tannins. This method is usually used for the heavy leathers such as sole leather, mechanical leathers, and saddle leathers. Shoe upper leathers and other lighter leathers are usually chrome tanned by immersion in a bath containing proprietary mixtures of basic chromium sulfate.

   Vegetable tanning is usually done in vats, principally due to longer process times, while chrome tanning takes place in drums or hide processors.

   In some cases, depending on type of leather being produced, hides are tanned in the tanhouse and later retanned as a part of the retan, color, fatliquor process. Where different tanning agents are used in the initial and retan steps, it is referred to as combination tanning.

   Waste effluents from the tanning process are substantial. Recycle of vegetable tan solutions is becoming more common in the industry; that which cannot be recycled may be used for retanning or evaporated and recovered. Recycle and recovery of chrome tanning solutions is also practiced at a few locations.

4. Splitting - The tanned hide is split to produce a grainside piece of essentially constant thickness and a flesh side layer. The flesh side layer or split can be processed separately or sold to split tanners.

RETAN, COLOR, FATLIQUOR PROCESS:

1. Retan - Retanning is done principally to impart different characteristics in the finished leather which it would lack if tanning were carried out in one step. Retanning may use chrome, vegetable, or synthetic tanning agents, and it is usually done in drums immediately preceding coloring and fatliquoring.

2. Bleaching - Bleaching hides with sodium bicarbonate and sulfuric acid after tanning is commonly practiced in the sole leather industry. Bleaching is done in vats or drums.

3. Coloring - Coloring is done in the same drums as retanning, and may be done either before or after fatliquoring. Natural dyes may be used, but many synthetic products are now available for this purpose.

4. Fatliquoring - Fatliquoring is the operation in which oils are added to replace the natural oils lost in the beamhouse and tanhouse processes and to make the leather pliable. The amount of oil added depends on the end use of the leather.

   Liquid wastes from the retan, color, and fatliquor process may be high volume-low strength compared with the other processes.

FINISHING PROCESS:

Finishing operations such as drying, wet-in coating, staking or tacking, and plating which follow the wet processes provide only minor contributions to the liquid waste primarily from cleanup of the paster drying plates and from paint spray booth water baths.

Trimmings are disposed as solid waste, and dust collected may be disposed in either wet or dry form.

Sheepskin Tannery Processes

Sheepskin tanning processes are somewhat similar to pigskin tanning in that generally there is no beamhouse process and degreasing is required. The three major processes are:

1. Tanhouse.

2. Retan, color, and fatliquor.

3. Finishing.

These processes and the sub-processes which take place during manufacturing are shown on Figure 2 and are described as follows:

TANHOUSE PROCESS:

1. Receiving - Most sheepskins are received at U. S. tanneries from both domestic and imported sources as pickled skins. These skins, which are salt cured, are normally tied in bundles of one dozen skins. These skins have had the wool removed at the packer or wool pullery and processed to the pickled condition. The wool pulling represents a beamhouse process.

   Skins tanned with the wool intact are referred to as shearlings. Tanning of these skins does not involve a beamhouse

process.

Pickled skins have been preserved for shipment and storage by immersion in a solution of brine and acid. Shearling skins are cured in a salt brine only. Excess solution is drained prior to bundling.

2. Storage - No special provision for storage is provided at most tanneries other than to keep the skins moist. There is some indication that pickled skins held for extended periods should be kept below 30°C (86°F) to avoid deterioration.

3. Fleshing - Skins from storage are taken from the bundle, inspected, and fleshed. Hides which have been fleshed prior to receipt at the tannery will usually be refleshed after tanning. Shearling hides are usually fleshed after a wash and soak operation. Fleshing is done on the same type of machine used for fleshing cattlehides. The skin is carried through rolls and across rotating spiral blades which remove the flesh from the skins.

   Fleshings and trimmings are normally collected and disposed of as a solid waste.

4. Degreasing - Skins are placed in drums, washed, and soaked, after which solvent or detergent is added in the same drums to remove grease.

   Grease is recovered as a by-product from those skins which have had the wool removed. When solvent degreasing is used, the solvent is recovered and reused.

   Skins with the wool on (shearlings) require substantially more water in the washing (scouring) operations and grease recovery is not normally practiced.

   There is a waste effluent from this process and a small amount of vapor, including solvent exhausted to the atmosphere.

5. Tanning - Sheepskins may be either chrome or vegetable tanned, although the majority are chrome tanned.

   Where the skins have been received at the tannery in the pickled condition, there are no liming or bating operations. Skins from the degreasing operation are placed in drums with salt water and proprietary mixtures of basic chromium sulfate for chrome tanning or solutions of the natural tannins for vegetable tanning.

6. Refleshing - In some cases, there is a refleshing operation following tanning, which produces a small amount of solid waste.

COLOR AND FATLIQUOR PROCESS:

1. Coloring - Skins to be colored are immersed in a dye solution in drums. Generally, synthetic dyes are used. Some bleaching may be done prior to coloring of shearlings.

2. Fatliquoring - This operation is performed in the same drum used for coloring. Skins are immersed in a solution containing various oils to replace the natural oils of the skin lost in the tanning process.

FINISHING PROCESS:

There are a number of operations which follow the coloring and fatliquor process, including drying, skiving, staking, carding, clipping, sanding, and buffing. These are essentially dry processes, and the only liquid waste contributed is from cleanup operations.

Solid wastes from the finishing operation include trimmings and skivings. Dust from the sanding and buffing operations may be collected dry and disposed of as a solid waste or wet and carried into the waste water system.

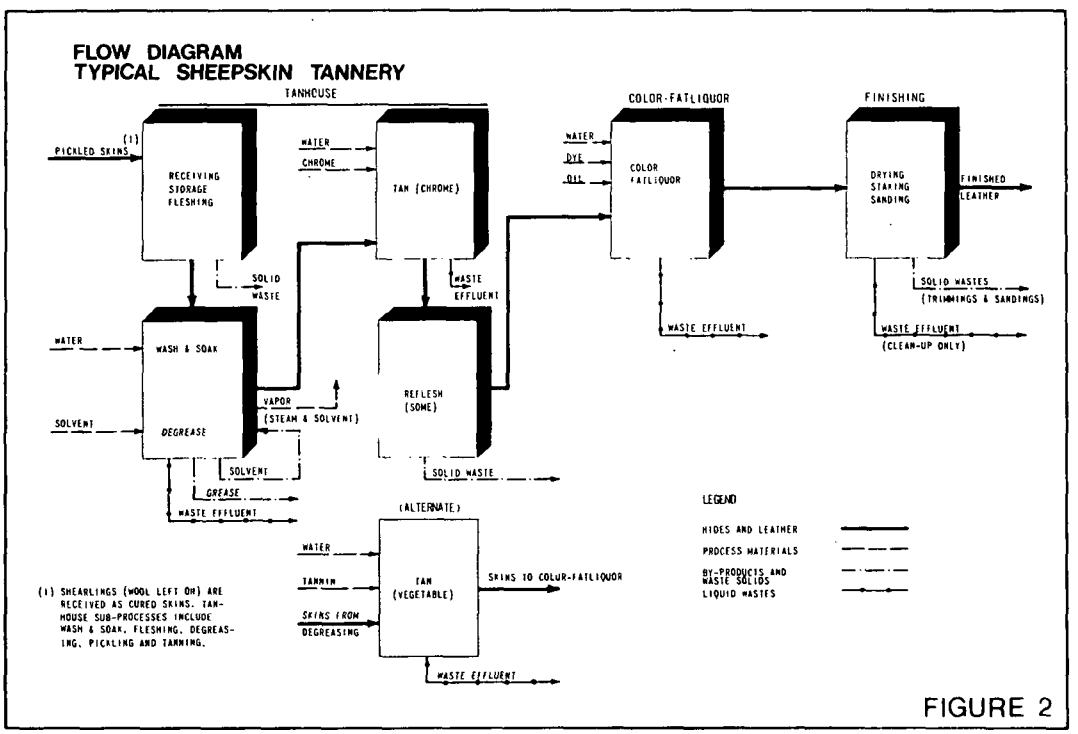

FLOW DIAGRAM
TYPICAL SHEEPSKIN TANNERY
TANHOUSE
COLOR-FATLIQUOR
FINISHING
(1)
PICKLED SKINS
RECEIVING
STORAGE
FLESHING
WATER
CHROME
TAN (CHROME)
WATER
DYE
OIL
COLOR
FATLIQUOR
DRYING
STAKING
SANDING
FINISHED
LEATHER
SOLID
WASTE
WASTE
EFFLUENT
SOLID WASTES
(TRIMMINGS & SANDINGS)
WASTE EFFLUENT
WASTE EFFLUENT
(CLEAN-UP ONLY)
WATER
WASH & SOAK
SOLVENT
DEGREASE
VAPOR
(STEAM & SOLVENT)
REFLESH
(SOME)
SOLVENT
GREASE
WASTE EFFLUENT
SOLID WASTE
(ALTERNATE)
WATER
TANNIN
SKINS FROM
DEGREASING
TAN
(VEGETABLE)
SKINS TO COLOR-FATLIQUOR
WASTE EFFLUENT
(1) SHEARLINGS (WOOL LEFT ON) ARE RECEIVED AS CURED SKINS. TANHOUSE SUB-PROCESSES INCLUDE WASH & SOAK, FLESHING, DEGREASING, PICKLING AND TANNING.
LEGEND
HIDES AND LEATHER
PROCESS MATERIALS
BY-PRODUCTS AND WASTE SOLIDS
LIQUID WASTES

FIGURE 2

Pigskin Tannery Processes

The pigskin tanning processes differ from cattlehide tanning in that there is essentially no beamhouse process, since most skins have the external hair removed at the packing house. Degreasing of the skins is a required tanhouse sub-process. The waste characteristics from pigskin tanneries are established from these three processes:

1. Tanhouse.

2. Color and fatliquor.

3. Finishing.

These processes and the operations which take place within each process are shown on Figure 3 and described as follows:

TANHOUSE PROCESS:

1. Receiving - Nearly all pigskins are received at the tannery either as fresh frozen skins or as brined refrigerated skins. They are usually tied in bundles of 40 to 50 pounds of skin. In some cases frozen skins may be in paper bags.

2. Storage - Refrigerated storage is used at most of the tanneries for skins which are to be held before tanning.

3. Degreasing - Solvent degreasing has been used by some pigskin tanneries. In this process, the skins are placed in drums, then washed and soaked in warm water to bring them up to a suitable temperature for degreasing. Solvent is added and the skins are tumbled to remove the grease. The solution of solvent, grease, and water is pumped from the drums to large tanks where some separation is achieved by decanting. From the tanks the solvent and grease is sent to a stripping column, where the solvent is recovered for reuse. Grease is recovered as a by-product.

   There is a waste effluent from this process, as well as a small amount of vapor, including solvent which is vented to the atmosphere.

   An alternate method, in which the skins are tumbled in hot water and detergent, has also been used. In this operation, grease is recovered by decanting or skimming it from the top of holding tanks to which waste is diverted prior to entry into the main plant sewer system.

4. Liming - From the degreasing operation the skins are placed in tanning drums with a lime slurry and sharpeners. The

purpcse of this is to remove the embedded portion of the hair from the skins.

5. Bating - The bating operation takes place in the same drums used for liming. The purpose of this operation is to delime the skins to reduce the swelling and remove any protein degradation products.

6. Pickling - The pickling operation follows the bating in the same drum. A sclution of brine and acid is used to bring the skins to an acid condition to prevent precipitation of chromium salts in the subsequent tanning process.

7. Tanning - Pigskin may be either chrome tanned or vegetable tanned. However, the only majcr tanner of pigskin in this country is using only the chrome tan process. Chrome tanning follows in the same drum used for pickling, using proprietary mixtures of basic chromium sulfate. Current practice is to fully tan the skins in this operation, eliminating any need for a retan operation at a later point.

8. Split and Shave - After tanning, the skins are tumble dried and then split and shaved or skived to obtain the desired thickness. The split part of pigskin has no commercial value as leather, and it is baled with other scrap and sold as a fertilizer component. The grain sides go to the color and fatliquor process.

COLOR AND FATLIQUOR PROCESS:

1. Coloring - Skins to be colored are immersed in a dye solution in drums. Generally, synthetic dyes are used.

2. Fatliquoring - This operation is performed in the same drum used for coloring. The skins are immersed in a solution containing varicus oils to replace the natural oils of the skin lost in the tanning process.

FINISHING PROCESS:

There are a number of operations which follow the coloring and fatliquor process, including drying, coating, staking, and sanding. These are principally dry processes, and the only liquid waste contributed is from cleanup operations. Where paster drying is used, there is some starch from the paste which is cleaned from the dryer plates. Water baths from spray booths may also represent minor sources of liquid waste.

Solid waste from the finishing operation includes trimmings, which are baled with the split and shave wastes for sale as

fertilizer. Dust collected from the sanding operation is disposed of as a solid waste.

FLOW DIAGRAM
TYPICAL PIGSKIN TANNERY

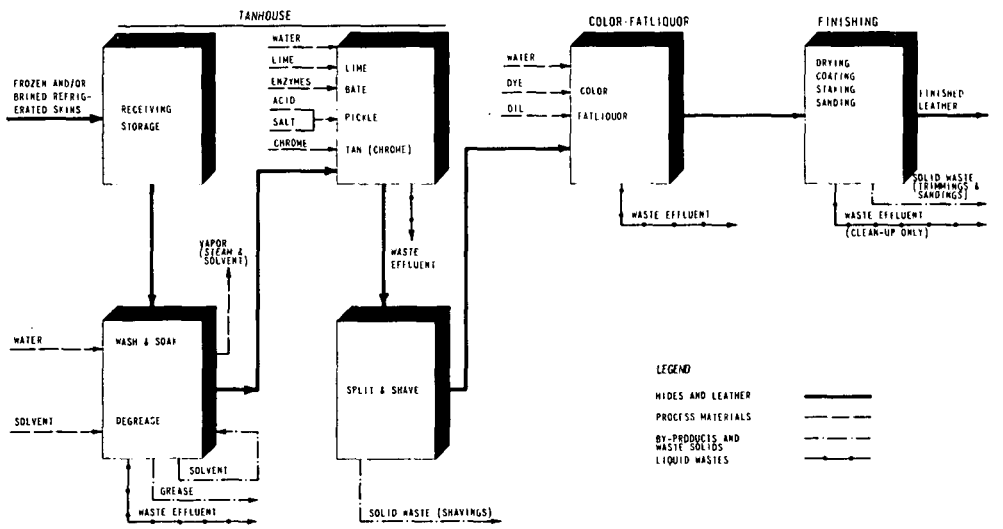


FIGURE 3

Classification System

As noted in the foregoing discussion on standard manufacturing processes, there are several variations in process steps. Under the system prepared by the Technical Committee on Standard Industrial Classification, sponsored and supervised by the Bureau of the Budget, the leather tanning and finishing industry bears SIC Number 3111.

A supplemental digit system reflecting the many variations in operations can further classify the industry. For purposes of this study, a four-digit system is recommended to reflect significant differences in processes. This matrix approach to the classification system provides flexibility and a rigorous means to encompass all process variables. The supplemental classification system is shown in Table 3. Some blank spaces are available if new processing techniques are developed.

Under this system, four digits appear to the right of a decimal point following the industrial classification. As shown in Table 1, these relate information by type of skin or hide, operations undertaken in the beamhouse, tanning method used, and type of material processed in the retan, color, fatliquor, and finishing steps.

TABLE 3

CLASSIFICATION SYSTEM
(3111.abcd)

Skin or Hide Type (a)	Beamhouse Operation (b)	Tanning Process (c)	Retan, Color, Fatliquor, Finishing (d)
1. Cattle	1. Pulp Hair	1. Chrome	1. Sides
2. Pig	2. Save Hair	2. Vegetable	2. Splits
3. Sheep	3. Hair Previously Removed	3. Alum	3. Sides and Splits
4. Deer	4. Hair Retained	4. Previously Tanned	4. Bends
5.	5. Wool Pullery	5. Vegetable and Chrome	5. Skins
6.	6. Hide Curing	6.	6.
7.	7. Pulp & Save	7.	7.
8.	8.	8.	8.
9. Other	9. Other and unknown	9. Other and unknown	9. Other
0. Various	0.	0. None	0. None

Several examples using the classification system for the more common processing methods are:

3111.1111 - Cattlehide (including calfskin), hair is pulped, chrome tanning process used, sides finished.

3111.1211 - Same as .1111 except hair is saved as a by-product.

3111.1221 - Same as .1211 except vegetable tanning process used.

3111.1110 - Same as .1111 except no retan, color, fatliquor, or finishing is done (tanning to blue stage only).

3111.1341 - Cattlehide, hair previously removed and hide pre-

viously tanned prior to receipt of hides at a finishing facility (finishing operations only).

3111.2315 - Pigskin, most hair removed prior to arrival of skin at tannery with small amount of residual hair pulped, chrome tanning process used, skins finished.

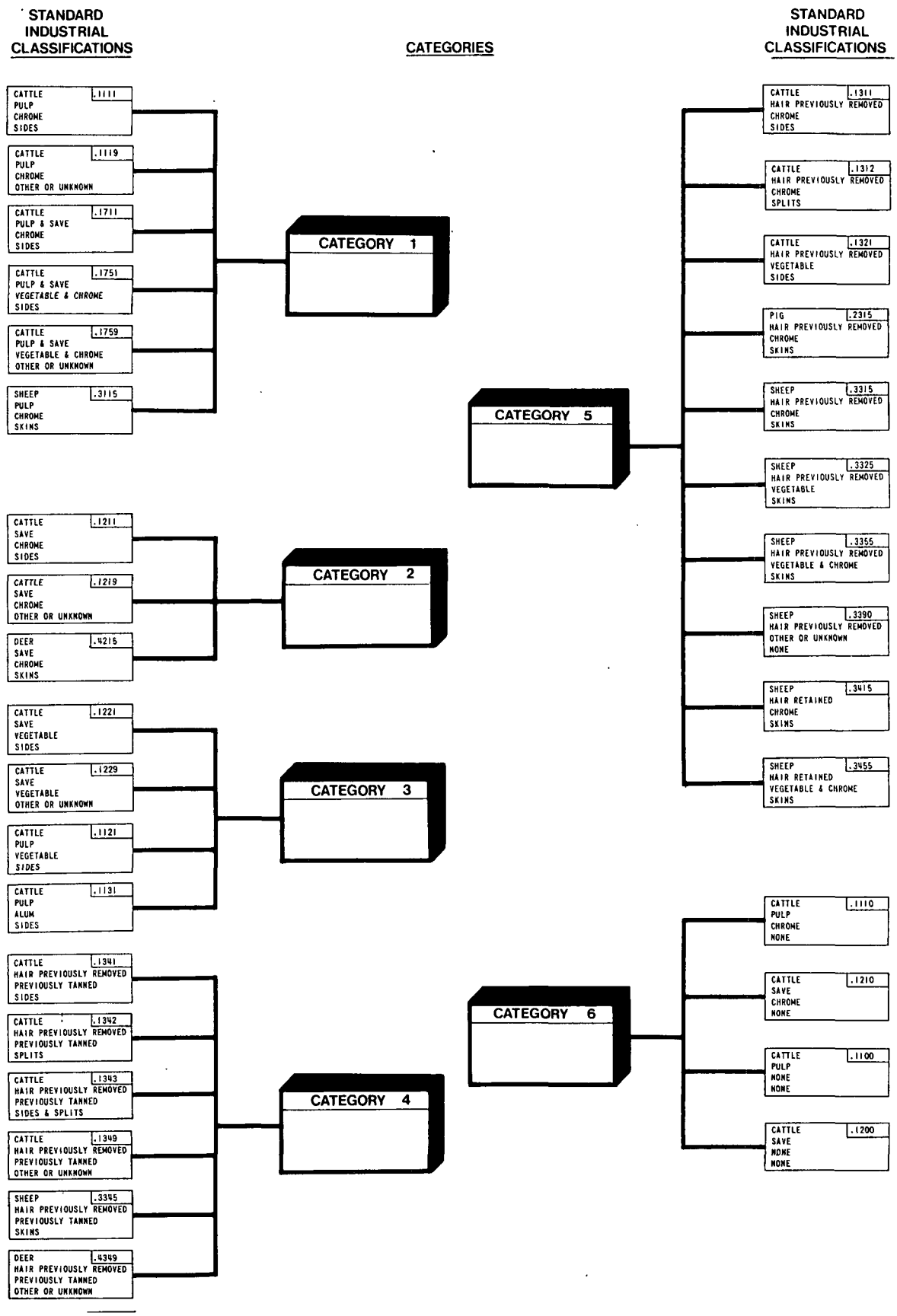
3111.3315 - Sheepskin, hair removed prior to receipt of skins at tannery, chrome tanning process used, skins finished.

3111.3415 - Same as .3315 except tanned with hair retained on the skin.

Categorization System

The tanning industry's present standard manufacturing processing techniques are covered with approximately 35 classifications which are combinations of the four basic digits that appear in Table 3. Based upon available data, these classifications were assessed for similarities in untreated waste water characteristics and processing techniques. This analysis results in grouping the classification into six major subcategories, as shown on Figure 4, for purposes of evaluating control and treatment technology. Each subcategory represents a common manufacturing process, as shown in Table 4.

These subcategories only identify operations that do not process a combination of hides or skins. Tanneries processing various types of hides or skins should be categorized on a prorated distribution basis. For example, a tannery that is pulping, chrome tanning, and finishing 90,000 pounds of cattlehides per day and chrome tanning and finishing 30,000 pounds of shearlings per day would have a categorized distribution of 75 percent and 25 percent in Subcategories 1 and 5, respectively. Thus, the suggested control and treatment guidelines presented later herein may be administered by various combinations of subcategories where appropriate.



CATEGORY SYSTEM
FIGURE 4

TABLE 4

PRINCIPAL PROCESSES OF SUBCATEGORIES

Subcategory	Primary Processes		
	Beamhouse	Tanning	Finishing
1	Pulp Hair	Chrome	Yes
2	Save Hair	Chrome	Yes
3	Save Hair	Vegetable	Yes
4	Hair Previously Removed	Previously Tanned	Yes
5	Hair Previously Removed or Retained	Chrome	Yes
6	Pulp or Save Hair	Chrome or no Tanning	No

SECTION V

WASTE CHARACTERIZATION

General

The first step in an appraisal of tannery liquid wastes is to define and quantify applicable waste constituents. These data must then be related to some unit of production. Information required to meet this need has been obtained from the following sources:

1. Correspondence with individual tanneries.

2. Information data sheets for individual tanners supplied through the Tanner's Council of America, Inc.

3. Corps of Engineers Permits.

4. Regulatory agency data summaries, including engineering reports on individual tanneries.

5. Literature review.

6. Sampling performed at selected tanneries.

7. Tannery visits.

Correspondence and information data sheets were received from over 140 wet processing firms. Corps permits for about 40 firms were submitted and sampling to verify waste characteristics was conducted at seven facilities. Information was also gathered from about five regulatory agencies and from visits to twelve tanneries other than those sampled. Data has been assembled on the basis of the various tannery subcategories.

Waste Constituents

Materials which can appear in tannery wastes include the following:

Hair	Lime	Sugars and starches
Hide scraps	Soluble proteins	Oils, fats, and grease
Pieces of flesh	Sulfides	Surface active agents
Blood	Amines	Mineral acids
Manure	Chromium salts	Dyes
Dirt	Tannin	Solvents
Salt	Soda ash	

The basic parameters used to define waste characteristics are as follows:

BOD5 (Five-day Biochemical Oxygen Demand)

COD (Chemical Oxygen Demand)

Suspended Solids

Total Nitrogen

Chromium

Oil and Grease (Hexane Solubles)

Sulfide

pH

Additional data from some sources permitted a check of the various forms of nitrogen and volatile components of total and suspended solids. No significant information was available on color. Information was also collected on total daily waste flow.

Unit Waste Quantities

Data was obtained for all parameters except water flow and pH in terms of concentrations (mg/l). When combined with waste flow records, this permitted computation of waste quantities in terms of weight of each waste constituent produced per day.

It is also necessary to define the quantity of each waste constituent generated per unit of production. Several measures of production were considered:

1. Weight of raw material processed.

2. Number of hides processed.

3. Weight of finished product.

4. Square feet of finished product.

Each of the above has some shortcomings when used as basis of production, as discussed below.

The weight of raw material includes varying amounts of dirt, manure, salt, and flesh. In some instances raw material may be green salted hides. In other cases it may be tanned hides in the "blue" stage.

Use of the number of hides includes all factors listed for hide weight. It also introduces a variance in weight. A tannery may be using a mixture of heavy and lightweight hides. Hides from winter reared animals tend to have a heavier hair coat.

Use of finished product as a unit of waste production is complicated by the industry's use of square feet as a measure in some instances and weight in others.

Weight of raw material processed has been selected as the best of the possible production parameters. The weight of raw material varies as some firms process salted hides, some utilize previously tanned hides as raw material, and other similar variations. All waste constituent data are related to the weight of the raw material as it enters a particular tannery or finishing facility.

Individual Process Contributions to the Waste

Each process in the production of the final product makes some contribution to the total waste load.

Hide Curing

Hide curing is not performed in the tannery, but rather in a packing house or in a separate hide curing facility. If it is performed in a separate facility it is considered to be a part of the tanning industry. The hide curing process consists of washing, curing, and often fleshing of the hides. Washing and curing are performed simultaneously in a tank containing a strong solution of salt. Subjecting the hides to contact with brine permits penetration of salt into the hide, resulting in moisture reduction and the inhibition of microbiological decomposition.

The brine solution is continually circulated and reused. Blowdown from the system is required to offset water gains from hide moisture losses. This blowdown also prevents the accumulation of foreign materials. Although the blowdown which constitutes most of the waste flow is quite small, the concentration of waste constituents is quite high. A typical characterization of this waste is as follows:

Table 5
Hide Curing

Waste Characteristics	Concentration (mg/l)	kg/1,000 kg Hide (lb/1,000 lb Hide)
BOD_5	15,610	3.9
COD	29,610	7.4
Total Solids	280,500	70.1
Suspended Solids	10,400	2.6
Oil and Grease	40,200	10.0
Water Use, l/kg (gal/lb)	0.24 (0.03)	

Tannery Processes

Processes which are an integral part of the tannery include the following:

Wash and Soak

Degreasing (sheepskin and pigskin)

Unhairing (sometimes followed by supplemental liming)

Bating

Pickling

Tanning (including bleaching for some vegetable tanning)

Retanning, Coloring, and Fatliquoring

Finishing

The waste contributions are described below:

Wash and Soak - This is the first wet process performed on the raw material as it begins the tanning process. The purpose of this operation is to remove salt, restore the moisture content of the hides, and remove any foreign material such as dirt or manure. If the raw material are brine cured hides, the hides are clean and the operation is one of salt removal. With green salted hides, manure and dirt must also be removed. The quantity of manure and dirt can vary widely, depending on the season of the year and the origin of the animal.

Primary waste constituents from the operation are BOD_5, COD, suspended solids, and total solids (including sodium chloride). Typical range in quantities for a cattlehide tannery with hair pulping and chrome tanning are as follows:

Constituent	kg/1,000 kg Hide (lb/1,000 lb Hide)
BOD_5	7-22
Suspended Solids	8-43
Total Solids	143-267

Following the wash and soak operation the hides are fleshed, if this has not been done previously. Fleshings are handled separately, and should not make a significant contribution to the liquid waste if handled properly. In some instances fleshing is performed after the unhairing and liming process.

Degreasing - Separate degreasing operations are not normally performed on cattlehide, but only on skins such as those from pigs and sheep. Two types of degreasing are used:

1. Hot water with detergent.

2. Solvent.

In both cases the grease is separated and recovered. However, some grease is not captured and enters the plant waste system. In the case of solvent degreasing, the solvent is also recovered. In addition to grease, BOD_5, COD, and suspended solids are other waste constituents.

The grease entering the plant waste system consists of only that portion which escapes the recovery process. In pigskin tanning, total grease removed from the skin can approach 100 kg (lb) per 1,000 kg (lb) of skins. The quantity entering the waste stream is only a small part of this. Unfortunately, reliable data on grease content of the waste stream is not available. The major problem arises from the difficulty in obtaining a truly representative sample.

Unhairing - Two processes are used for unhairing:

1. Hair save.

2. Hair pulp (or hair burn).

In the hair save operation, the hair is loosened for subsequent machine removal. Lime and sharpeners (sodium sulfhydrate, etc.) are used to perform this function. The waste is characterized by a high alkalinity, pH, sulfide, and nitrogen content. The nitrogen content results from the reaction of the unhairing solution with the protein matter. Other constituents of the waste include COD, BOD_5, suspended solids, and total solids. A part of the soluble solids is sodium chloride not removed in the soak and wash.

An additional step in the hair save operation is machine removal of hair from the hide. Although the hair is handled as a solid by-product, it does require washing prior to baling and sale as a marketable product. The waste water from washing contains the same waste constituents as the unhairing solution, only in a more diluted concentration.

The hair pulping operation is similar to that of hair saving except that higher chemical concentrations are used, particularly with respect to the sharpeners. In this process the proteinaceous hair is solubilized sufficiently to disperse it in the processing liquid. The waste water, therefore, has a higher content of waste constituents, particularly with respect to sulfides and nitrogen.

For a cattlehide chrome tannery, BOD_5 content of the waste from the hair save process will range from 17 to 58 kg (lb) per 1,000 kg (lb) of raw material. With the hair pulping process this may be 53 to 67 kg (lb). Likewise, the total nitrogen content of the hair save waste will be substantially less than the 11 to 15 kg (lb) per 1,000 kg (lb) experienced with the hair pulp process.

Bating - The purposes for the bating process are to delime, reduce swelling, peptize the fibers, and remove protein degradation products. Major chemical additions are ammonium sulfate to reduce pH to a controlled level and an enzyme to condition the protein matter. The reaction of lime with ammonium sulfate produces calcium sulfate. The total nitrogen content of the waste is 5 to 8 kg (lb) per 1,000 kg (lb) of hide with ammonia nitrogen constituting about two-thirds.

Pickling - The purpose of the pickling operation is to prepare the hides for the tanning process. In vegetable tanning, pickling may be omitted. Pickle solutions contain principally sulfuric acid and salt, although a small amount of a wetting agent and biocide are sometimes used. Since protein degradation products, lime, and other waste constituents have been previously removed, the quantity of BOD_5, suspended solids, and nitrogen are low. Principal waste constituents are the acid and salt. The strong liquor dump after processing is a source of waste since the hides are normally not rinsed prior to tanning.

Tanning - The purpose of the tanning process is to produce a durable material from the animal hide or skin which is not subject to degradation by physical or biological mechanisms. This is accomplished by reaction of the tanning agent with the hide collagen. Chrome and vegetable tanning are the two principal processes, although other materials such as alum, and other metal salts and formaldehyde can be used.

In the chrome process a basic chromic sulfate or a proprietary chrome tanning solution is used. Other process solution constituents include sodium formate, and soda ash. The chromium must be in the trivalent form and in an acid media to accomplish desired results. Some tanneries prepare chrome tanning by reducing sodium dichromate solution to the trivalent form, using glucose as a reducing agent. The waste from this process is the principal source of trivalent chrome in the plant waste. The only potential entry of hexavalent chromium into the waste system comes from spillage.

The spent chromium tanning solution is relatively low in BOD_5 and suspended solids.

Waste from a vegetable tanning process is quite different. The reaction rate of vegetable tan with the hides is much slower than that of chrome tanning solution. Because of the longer contact time, the process is normally carried out in vats with some type of gentle agitation. In some instances the hides are passed through a series of vats with varying solution strength. Because of the cost of tanning materials, process solution conservation has been practiced. Therefore, that part of the solution entering the waste system is due to drag-out or planned blowdown to maintain tanning solution quality. Vegetable tannin in the waste is a source of both BOD_5 and color.

Retan, Color, Fatliquor - Retanning, coloring, and fatliquoring are normally performed in drums. The chrome or vegetable tanned hides are placed in the same drums and all three processes are performed on the hides before they are removed.

The retan process is performed to provide added tanning solution penetration into hides after splitting. Chemicals used for retanning can be chrome, vegetable, or synthetic tanning agents. Because of the

low concentrations of chemicals in the retan process, the concentration of the waste water is not strong; usually this process does not add a significant quantity to the total waste flow.

The most varying process in the tannery is coloring. There are hundreds of different kinds of dyes, both synthetic and vegetable. Synthetic dyes are the most widely used in the industry. When synthetic dyes are used, acid is usually added in order to provide a better uptake of dye into the leather. Normally, vegetable tanned leathers are not dyed in this manner. If the vegetable tanned leather is colored, it is generally surface dyed by spraying the color on the leather surface.

The fatliquoring operation can be performed either before or after coloring. There is a wide range of type and amount of oil added in this process, depending upon the end use of the leather.

Liquid waste from the retan, color, and fatliquor operations may be high volume-low strength compared with the beamhouse and tanhouse.

The temperature of the retan, color, and fatliquor waste flows is generally high--above 37.7°C (100°F). The major treatment concern of the retan, color, and fatliquor waste is removal of color and oil. These two constituents can be kept to a minimum by utilizing chemical concentrations that provide for the best uptake of the chemicals into the hide. Because of the color in the waste water, recycling is not normally practiced. Use of high temperatures in retanning will enable maximum uptake of chromium and reduce the discharge of this constituent.

Finishing

The finishing processes represent the lowest water flows of the tannery because they are primarily dry processes. There are some wet processes such as minor wetting operations to make the hide handle more easily in the staking or tacking operations. The pasting operation also uses small amounts of water. However, several tanneries report reusing paste mixtures; therefore, it does not flow into the waste stream. This pasting water is water mixed with starch; thus, it is quite high in concentration even though the volume is very low.

Total Plant Liquid Waste

The quantity of waste water is important to the economics of treatment in that a number of the unit operations performed in treatment are designed totally or partially on a hydraulic basis. In addition, water conservation can often reduce the quantity of processing chemicals used which later become constituents requiring removal in treatment processes. Also, process solution reuse practices such as that for tanning not only reduce waste flow but also eliminate the major part of a waste constituent from the total plant waste stream.

An appraisal was made to determine the quantity of waste flow from tanneries in each of the six subcategories defined previously. A typical plot of waste water flow versus tannery production is shown in Figure 5 for Subcategory 1. The random nature of the data is obvious. It is apparent that size of facility is not a factor for low waste water flow. These waste water quantities are characterized in Table 6 by the median, mean, and mode for each subcategory. Definitions of these terms are as follows:

Median - The number of tanneries having waste flows lower than this value is equal to the number of tanneries having waste flows higher than this value.

Mean - This is the average value determined by adding waste flow data for all tanneries and dividing by the number of tanneries.

Mode - This is the mid-point of the one-gallon interval in which the most frequent occurrence of waste water flow occurs. This measure is not too significant since frequency of occurrence in any one interval was not generally too much greater than adjacent intervals. Use of a wider interval would have reduced significance of this measure.

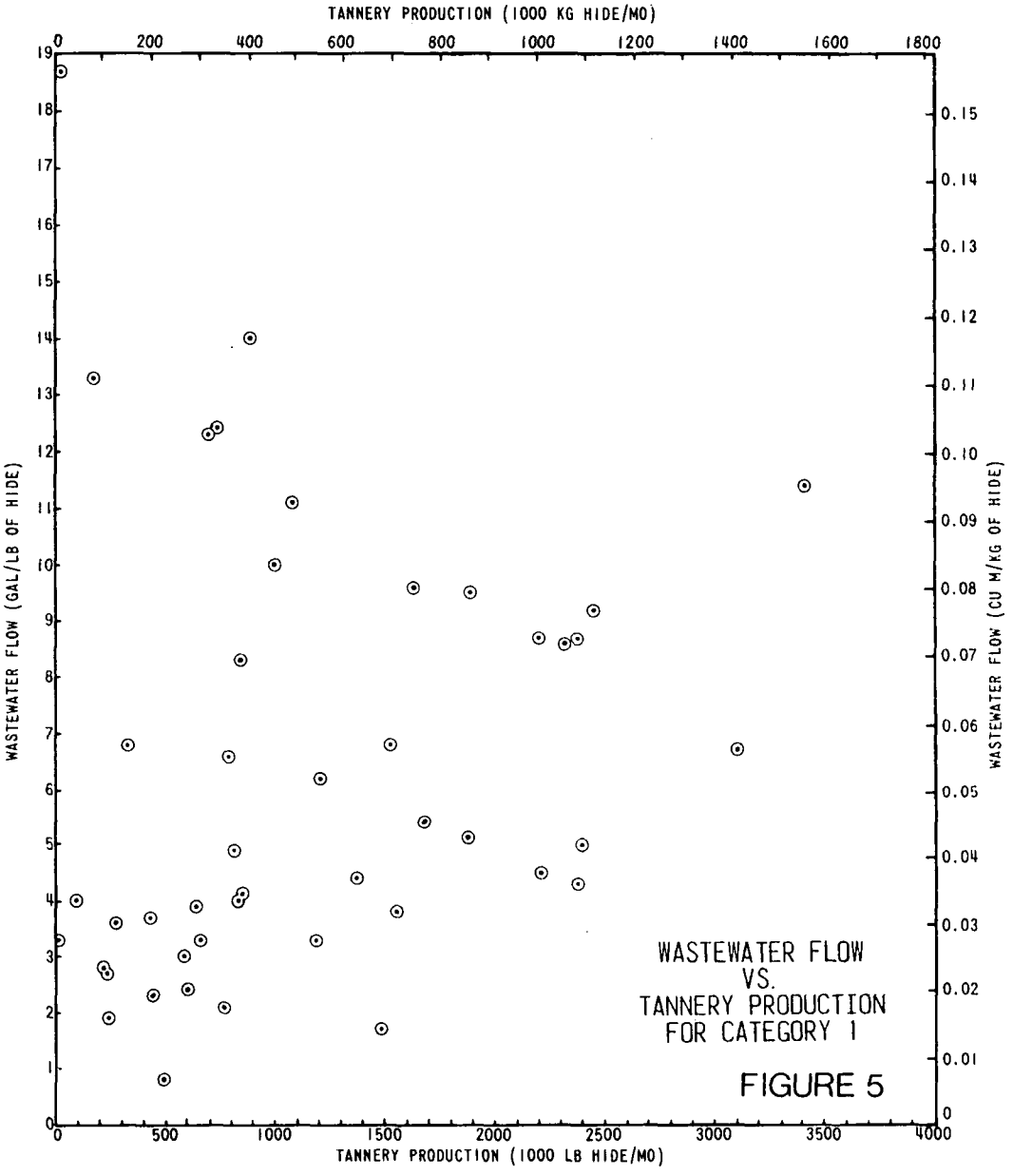

TANNERY PRODUCTION (1000 KG HIDE/MO)
0
200
400
600
800
1000
1200
1400
1600
1800
WASTEWATER FLOW (GAL/LB OF HIDE)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
WASTEWATER FLOW (CU M/KG OF HIDE)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.12
0.13
0.14
0.15
0
500
1000
1500
2000
2500
3000
3500
4000
TANNERY PRODUCTION (1000 LB HIDE/MO)
WASTEWATER FLOW
VS.
TANNERY PRODUCTION
FOR CATEGORY 1

FIGURE 5

TABLE 6

WASTEWATER QUANTITIES

Category	Waste Flow, cu m/kg of hide (gal/lb of hide) Median	Mean	Mode	Range	No. of Tanneries	Used Later Herein for Economic Analysis, cu m/kg of hide (gal/lb of hide)
1	0.040 (4.8)	0.053 (6.4)	0.029 (3.5)	0.007-0.156 (0.8-18.7)	46	0.033 (4.0)
2	0.050 (6.0)	0.063 (7.6)	0.050 (6.0)	0.001-0.189 (0.1-22.6)	14	0.050 (6.0)
3	0.044 (5.3)	0.050 (6.0)	0.021 (2.5)	0.007-0.106 (0.8-12.7)	16	0.042 (5.0)
4	0.017 (2.0)	0.020 (2.4)	0.017 (2.0)	0.003-0.033 (0.3-3.9)	10	0.017 (2.0)
5	0.050 (6.0)	0.063 (7.6)	0.082 (9.8)	0.006-0.204 (0.7-24.4)	20	0.063 (7.5)
6	---	0.028 (3.4)	---	0.014-0.056 (1.7-6.7)	3	0.017 (2.0)

Although data are quite random for any subcategory, there is a trend toward distinct levels for each one. The randomness of the data is due not only to differences in process operations but also to the non-scientific methods used to gage and sample waste streams in the tanning industry. To determine a waste flow value for use as the basis of treatment, facility needs, and economics, it was necessary to take into consideration the basic data for individual tanneries in addition to that shown in Table 6. It was reasoned that the design basis should generally be equal to or less than the median, but in no case greater than the mean. This approach was used on the basis that if 40 to 50 percent of the tanneries of a similar type could meet processing needs at a particular level, others could also meet this value through attainable conservation measures. This was prompted by observations made on plant visits that many tanneries use excess water by constantly running wash-down hoses to waste, by unmetered and poor control of water used for washing and rinse operations and by other similar practices.

Characteristics of Total Plant Waste Flows

An attempt was made to rigorously define flow and the concentration of waste constituents from each step in the tanning process. This was not possible due to lack of reported data and to the difficulty of isolating all of the individual flows during the plant testing program made as a part of these studies. Therefore, a comprehensive assessment of total plant wastes is increasingly important.

A summary of raw waste characteristics for each subcategory is shown in Table 7. The data have been classified as received and no further attempt is made toward explanation of inconsistencies with some information. Detailed information for individual tanneries is presented as a part of the documentation submitted as a supplement to this report. The sources of this information have been described previously.

Examination of the information indicates the following:

1. Most data show a wide variance in values.

2. Based on average values, some quantities appear to be high or low.

Typical variance is illustrated by the BOD_5 for Subcategory 1, where the range in values is 4.8 to 270 kg (lb) with an average of 95 kg (lb) per 1,000 kg (lb) of hides. The variance of this and other parameters is undoubtedly due partially to some difference in processing techniques among tanneries and partially to lack of analytical accuracy. However, it is probable that a major part of the difference is due to the variations in waste quality associated with the multiplicity of waste discharge patterns which can exist and the sampling methods. Berthouex and Brown (5) utilize a Monte Carlo simulation to characterize many possible combinations of tannery process solution discharges. This

waste variance, along with the shortcomings of the normal time spaced proportional flow waste increment method of composite sample preparation, are the principal contributions to variance. If incoming waste were to flow to an equalization tank with a relatively constant outflow, it can be reasonably assumed that variance would have been decreased significantly.

In examination of average values for various parameters, the sulfide content of the waste for Subcategory 2 appears low, even though this is a hair save operation. Also, the chromium content appears high for Subcategory 4 where only some retanning is performed. The average chromium content is 60 percent of that for a complete chromium tannery process, as shown in Subcategory 1. Other such apparent inconsistencies occur and unusual average values result since information from only one or two tanneries is available.

Analyses were made of the size of plants in each industrial subcategory, and a typical plot for Subcategory 1 is shown in Figure 6. Production capacity coupled with waste water flows are used later herein to assess the economics of waste treatment.

Raw and treated waste characteristics were also assessed for each subcategory in relation to the size and age of tanneries. No significant relationship is observed. For example, some old, small tanneries produce effluents of better quality than those which are new and large; the opposite case is also noted.

TABLE 7

RAW WASTEWATER

CHARACTERISTICS BY CATEGORY

	Raw Wastewater Characteristics, kg/1,000 kg of Hide (lb/1,000 lb of Hide)*								
	Category No. 1			Category No. 2			Category No. 3		
Characteristics	No. of Tanneries	Range	Average	No. of Tanneries	Range	Average	No. of Tanneries	Range	Average
Flow: cu m/kg (gal/lb)	46	0.007-0.156 (0.8-18.7)	0.053 (6.4)	14	0.001-0.189 (0.1-22.6)	0.063 (7.6)	16	0.007-0.106 (0.8-12.7)	0.050 (6.0)
BOD_5	24	4.8-270	95	9	22-140	69	12	7.4-130	67
COD	18	10.5-595	260	7	88-215	140	9	24-695	250
Total Solids	16	36-890	525	7	140-900	480	9	120-800	345
Suspended Solids	23	6.7-595	140	9	30-350	145	10	20-445	135
Total Chromium	18	0.1-19	4.3	7	0.3-12	4.9	5	0.2-0.6	0.2
Sulfides	12	0.1-46	8.5	4	0.1-2.8	0.8	7	0.1-4.2	1.2
Grease	13	0.1-70	19	5	0.7-105	43	7	0.1-160	33
Total Alkalinity (as $CaCO_3$)	12	0.5-300	98	1	62-85	72	6	4.1-135	66
Total Nitrogen (as N)	7	3.1-44	17	6	3.6-22	13	5	0.9-23	9.2
pH	26	1.0-13.0	--	8	4.0-12.6	--	12	2.0-13.0	--
Temperature**: °C (°F)	15	2.8-93.2 (37-200)	21.1 (70)	6	1.7-27.8 (35-82)	18.3 (65)	3	4.4-28.9 (40-84)	17.2 (63)

*Except pH; flow in cu m/kg (gal/lb), and temperature in °C (°F).

**Average temperature is average summer and winter values; temperature range is low winter to high summer values.

TABLE 7 (Continued)

RAW WASTEWATER

CHARACTERISTICS BY CATEGORY

Raw Wastewater Characteristics, kg/1,000 kg of Hide (lb/1,000 lb of Hide)*

Category No. 4			Category No. 5			Category No. 6		
No. of Tanneries	Range	Average	No. of Tanneries	Range	Average	No. of Tanneries	Range	Average
10	0.003-0.033 (0.3-3.9)	0.020 (2.4)	20	0.006-0.204 (0.7-24.4)	0.063 (7.6)	3	0.014-0.056 (1.7-6.7)	0.028 (3.4)
3	6.7-67	37	8	10-140	67	2	32-160	110
3	5.7-63	28	5	11-265	170	2	53-155	230
2	47-285	140	7	52-980	490	2	210-910	595
3	7.0-125	47	8	3.1-865	88	2	44-185	110
3	0.4-4.8	2.6	7	0.1-2.1	1.2	1	3.8-5.9	4.4
1	2.1	2.1	1	4.5	4.5	1	2.0-6.3	3.7
3	2.2-19	7.9	7	0.6-46	24	2	1.0-19	6.6
1	39	39	3	6.6-180	69	1	37-54	43
2	0.8-6.5	3.7	5	0.6-29	6.0	1	14-18	16
3	3.4-11.2	--	9	1.5-12.5	--	2	9.2-10.4	--
3	10.0-26.6 (50-80)	20.7 (69)	3	4.4-36.6 (40-98)	22.8 (73)	--	-- --	-- --

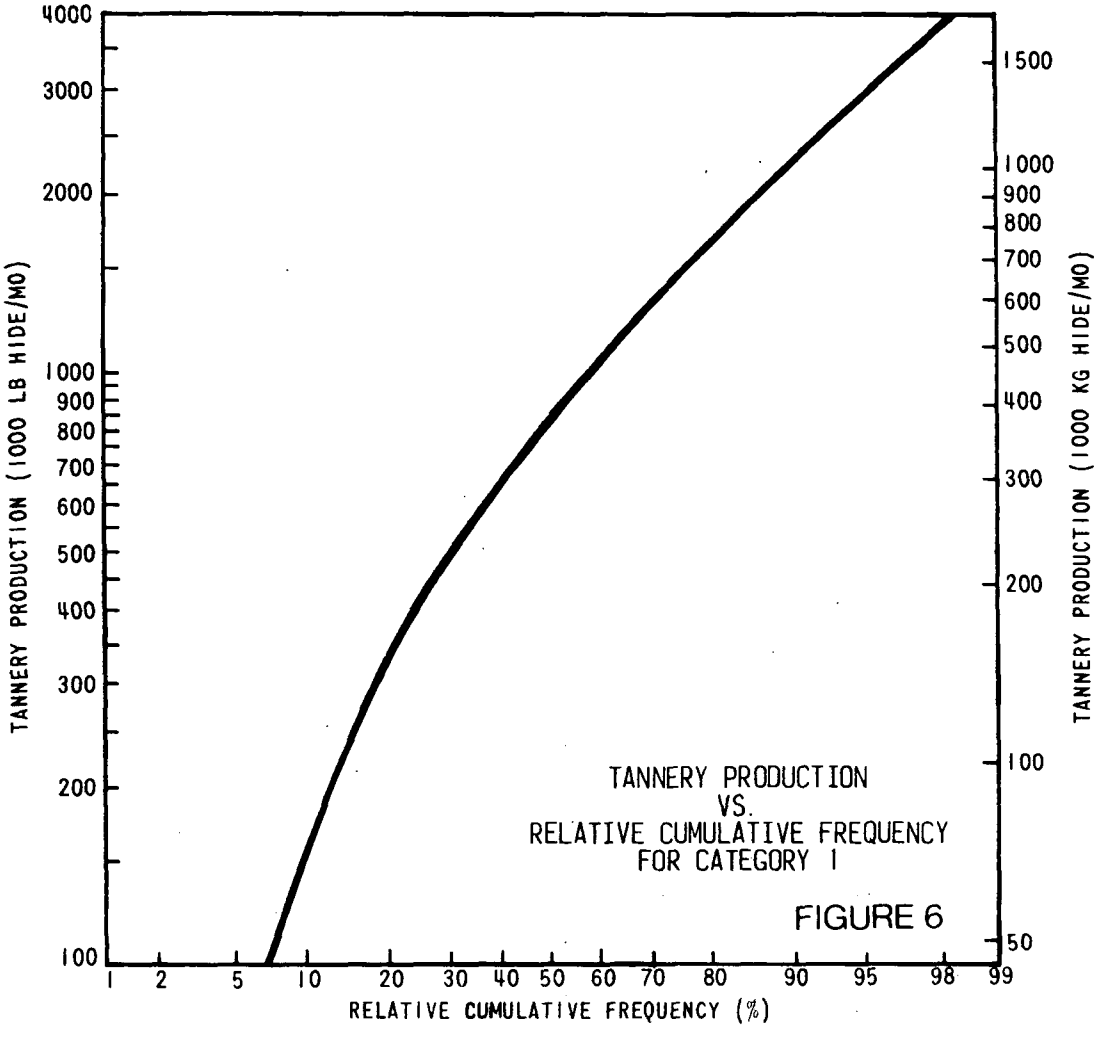

4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
TANNERY PRODUCTION (1000 LB HIDE/MO)
1500
1000
900
800
700
600
500
400
300
200
100
50
TANNERY PRODUCTION (1000 KG HIDE/MO)
1 2 5 10 20 30 40 50 60 70 80 90 95 98 99
RELATIVE CUMULATIVE FREQUENCY (%)
TANNERY PRODUCTION
VS.
RELATIVE CUMULATIVE FREQUENCY
FOR CATEGORY 1

FIGURE 6

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

WASTE WATER PARAMETERS OF MAJOR SIGNIFICANCE

A thorough analysis of the literature, industry data and sampling data obtained from this study, and EPA Permit data demonstrates that the following waste water parameters are of major pollutional significance for the leather tanning and finishing industry:

Biochemical Oxygen Demand (5-day, 20°C., BOD_5)
Total Chromium
Grease Fats and Oils
Sulfide
Suspended Solids (SS)
Total Kjeldahl Nitrogen
Fecal Coliforms
pH

Rationale for Selection of Major Parameters

Biochemical Oxygen Demand (BOD_5) - This parameter is an important measure of the oxygen utilized by microorganisms in the aerobic decomposition of the wastes at 20°C over a five day period. More simply, it is an indirect measure of the biodegradability of the organic pollutants in the waste. BOD_5 can be related to the depletion of oxygen in a receiving stream or to the requirement for waste treatment.

If the BOD_5 level of the final effluent of a processing plant into a receiving body is too high, it will reduce the dissolved oxygen level in that stream to below a level that will sustain most fish life; i.e. below about 4 mg/l. Many states currently restrict the BOD_5 of effluents to below 20 mg/l if the stream is small in comparison with the flow of the effluent. A limitation of 200 to 300 mg/l of BOD_5 is often applied for discharge to municipal sewer, and surcharge rates often apply if the BOD_5 is above the designated limit.

Total Chromium - Most of the leather produced in the U. S. is tanned with chromium salts. Chromium, in some forms, can be harmful to aquatic life and, therefore, is an important parameter to be identified. There is evidence to indicate that chromium in both the trivalent and hexavalent state is harmful, and thus the total chromium parameter should be used.

Grease - The grease analysis measures different types of materials, including oils, fats, and other such materials commonly found in tannery waste waters. Sources of grease from tanneries are from both the animal fat on the hides, as well as oils added to the hide during the fatliquor

process. The grease is usually all of nonpetroleum origin. Large amounts of oil and grease can be detrimental to surface waters by retarding stream reaeration. In addition, large amounts of oil and grease are unsightly and biological degradation may result in odor problems.

Sulfide - A significant portion of alkaline sulfides contained in tannery waste water can be converted to hydrogen sulfide at a pH below 8.5 to 9.0, resulting in the release of this gas to the atmosphere. This gas is odorous, and can result in property damage through paint discoloration. In sewers, hydrogen sulfide can be oxidized to sulfuric acid, causing "crown" corrosion. At higher concentrations this gas can be lethal. This is particularly significant as a hazard in sewer maintenance. Sulfide compounds are used extensively in the beamhouse for the unhairing process, and thus are found in tannery effluents.

Suspended Solids (SS) - Material found in suspended form in tannery wastewaters consist primarily of proteinaceous substances (flesh, hide, or hair) and insoluble waste chemicals. Suspended solids are an important measure of the pollutional significance of tannery wastes, since they generally exert a BOD_5 and can also result in detrimental sludge deposits in streams and lakes.

Total Kjeldahl Nitrogen - Total kjeldahl nitrogen (TKN) is ammonia nitrogen plus organic nitrogen content in waste water. Hence, TKN measures the major nitrogen impact upon a waste treatment plant or stream. This parameter is thus an important measure of the potential environmental impact of tannery waste water.

Fecal Coliforms - Microbiological testing for the presence of fecal coliforms will indicate the potential for the waste water to contain pathogenic bacteria. Since many tanneries have sanitary sewage facilities connected into the industrial waste sewer system, the fecal coliform parameter is an important parameter.

pH - The pH of tannery waste is dependent upon the type of process employed. For example, tanneries with beamhouse operations generally exhibit raw waste with a pH in excess of 10. Tanneries without a beamhouse operation will usually discharge at a pH around 4 to 5 due to the acid condition of the tan material. Either high or low pH conditions may inhibit growth of stream flora. Thus, pH is an important parameter to evaluate the impact of the waste on the environment.

Rationale for Selection of Minor Parameters

Chemical Oxygen Demand (COD) - COD is another measure of oxygen demand. It measures the amount of organic and some inorganic pollutants under a carefully controlled direct chemical oxidation by a dichromate-sulfuric

acid reagent. COD is a much more rapid measure of oxygen demand than BOD_5 and is potentially very useful.

COD provides a rapid determination of the waste strength. Its measurement will indicate a serious plant or treatment malfunction long before the BOD_5 can be run. A given plant or waste treatment system usually has a relatively narrow range of COD: BOD_5 ratios, if the waste characteristics are fairly constant, so experience permits a judgment to be made concerning plant operation from COD values. In the industry, COD ranges from about 1.6 to 10 times the BOD_5; the ratio may be to the low end of the range for raw wastes, and near the high end following secondary treatment when the readily degraded material has been reduced to very low levels.

In summary, BOD and COD measure organic matter which exerts an oxygen demand. Both COD and BOD are useful analytical tools for the processor. However, no COD effluent limitations are required because BOD limitations have been established.

Total Solids - Total solids is a valuable parameter, since it measures both suspended and dissolved solids in the waste. Since tannery wastes are high in dissolved solids, the total solids test is an effective parameter to assess the impact of dissolved materials. The largest portion of the dissolved solids are sodium chloride and calcium sulfate. Sodium chloride comes principally from removal of salt from the raw hides by washing, and also from salt added in the pickling operation. Calcium sulfate can come from several locations in the tannery, but principally from the reaction of residual ammonium sulfate and sulfuric acid with lime used in the unhairing process. Dissolved solids are particularly important for consideration of recycle systems, and also for potential impact on stream life and water treatment processes. Total solids limitations are not established for tanneries because of insufficient information.

Ammonia Nitrogen - The principal sources of ammonia in tannery wastes are the ammonium sulfate used in the bating process and that which results from decomposition of organic nitrogen. Ammonia limitations are not needed because total kjeldahl nitrogen limits require the control of ammonia.

Color - Color from a tannery results principally from the chrome or vegetable tan liquor and various dyes and paints used during coloring operations in the production of the leather. The contribution by vegetable tan is by far the greatest. Excessive color may inhibit the activities of some aquatic life, but it is primarily of concern from an aesthetic standpoint. There is not sufficient information at this time to establish color limitations.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

General

Waste treatment practices in the leather tanning and finishing industry vary widely. Some tanneries use no treatment or only simple screening. Others have employed activated sludge, trickling filters, spray irrigation, and lagoon systems to achieve treatment needs. The degree of treatment which the waste receives has been determined by three factors:

1. Type of receiving system.

2. Quality criteria of the receiving system.

3. Tannery processes.

Effluent quality requirements for a tanner discharging to a municipal sewer have been less stringent than those for a tanner discharging to a stream, lake, or ocean. Therefore, those systems providing a higher degree of treatment are associated with tanneries discharging directly to bodies of water.

Variations in treatment schemes are also due to the differences in raw waste characteristics associated with processing hides into different types of leather. Although the basic unit operations are the same, variations in sub-unit processes create a variance in both effluent quantity and quality. These differences are attributed to the need to obtain different finished leather characteristics and the general attitude of tanneries to produce the desired leather quality without regard to conservation of process chemicals and water.

Based upon communication with around 140 wet processing firms in the industry, approximately 60 percent of the tanneries discharge to municipal systems. Analysis of these same data indicates that tanneries discharging to municipal sewers also represent about 60 percent of productive capacity. This group includes those discharging without treatment into municipal systems, as well as those providing pretreatment prior to the conveyance to a municipal facility. With increasing effluent restrictions imposed by municipal systems, there is a trend toward at least some pretreatment by all tanneries.

The survey of tanners and finishers indicated few (21) have on-site biological waste treatment facilities. Of those employing biological treatment, three have activated sludge plants while fifteen have lagoons of aerobic and aerobic-anaerobic operating capabilities. Trickling filters are utilized in three treatment schemes. Advanced treatment

facilities are non-existent. Some pilot studies of reverse osmosis and activated carbon have been made, but without well defined results. Filtration and ion exchange have not been tested on tannery effluent.

Solids handling and disposal typically have had secondary significance at tannery waste treatment facilities. Since on-site disposal in open dumps prevails, sludge and other waste solids have not in the past had proper disposal, Sludge handling is receiving more emphasis. Pressure filters, vacuum filters, and centrifuges are presently utilized for dewatering sludge prior to land disposal.

In-plant waste control procedures have included efforts by some tanneries to conserve water and materials. A number of tanneries have intensified housekeeping practices to minimize the entry of solid wastes into the sewer. Development of hide processors (concrete mixers) has greatly influenced water usage in applicable wet processing operations. This equipment requires a smaller float (processing solution) than vats, paddles, or drums.

The potential for materials conservation has not been fully realized, particularly in the beamhouse operations. Recycle and recovery techniques have generally been applied only in those areas where direct cost savings are demonstrated. Such practices are tannin and chromium reuse. Plans for reuse of some portions of treated waste streams are in the conceptual stages at several tanneries.

Basis of Tannery Waste Treatment

The following is a summary of approaches which can be used to achieve various levels of tannery waste control and treatment:

1. In-process methods of reducing waste.

    a. Water conservation.

    b. Process solution reuse or recovery.

    c. In-plant treatment to remove a waste constituent.

2. Preliminary Treatment.

    a. Disposal to a municipal system or additional unit operations for further treatment.

    b. Adjustment of pH, alkalinity, and/or acidity to required levels.

    c. Removal of chromium, sulfides, hexane solubles, and toxic materials to levels which will not pass through or harmfully affect subsequent treatment.

d. Partial removal of BOD_5, COD, suspended solids, and total nitrogen.

3. Major reduction of BOD_5 and suspended solids.

   a. Removal of BOD_5 and suspended solids to levels of less than 50 mg/l.

   b. Some additional nitrogen removal beyond that provided by preliminary treatment.

   c. Normal treatment configuration includes some type of biological process followed by effective removal of suspended solids.

4. Major reduction of all forms of nitrogen.

   a. Reduction of total nitrogen to a level of about 10 mg/l or less.

   b. Treatment follows biological treatment for BOD_5 removal.

   c. Treatment steps include an aerobic biological process followed by an anaerobic biological process. Each process is followed by a clarifier for sludge removal.

5. Major removal of all waste constituents.

   a. Follows previously described biological and settling processes for removal of BOD_5, suspended solids, and nitrogen.

   b. Filtered waste enters reverse osmosis process (or electrodialysis process) for removal of remaining organic constituents, as well as major quantities of dissolved salts such as sodium chloride.

   c. Waste stream is directed to evaporators for concentration for final disposal.

   d. Product water is of low solids content suitable for reuse.

6. Waste treatment for hide curing facilities.

   a. The high strength of this waste requires special considerations.

   b. Treatment for all levels except pretreatment requires

direct incineration of total waste or solar evaporation in arid areas.

An analysis covering the application for each of these approaches is described later herein. Such an analysis also sets forth in more detail the technical and economic considerations involved.

In-Process Methods of Reducing Waste

In an appraisal of any plant waste production, the manufacturing cycle must first be investigated to determine any modifications which can reduce the waste flow and the concentration of waste constituents. Particular emphasis must be given to reducing those factors which would pose problems in treatment of the total waste. In some instances, reuse or recovery of materials from process solutions can produce economies which will at least partially offset costs.

It is not possible to identify every point in the hide preparation and tannery processes where a modification would reduce waste quantities. Tanning formulas and processing steps are developed by experience. Implementation of many potential waste reduction steps are contingent upon the effect on the manufactured product.

The assessment of in-house conservation and treatment is considered from the following approaches:

1. Water conservation.

2. Process solution reuse or recovery.

3. In-plant treatment to remove a specific waste constituent.

By reference to Table 6, it is noted that water use per unit weight of hides processed varies significantly in all subcategories. The variations for three subcategories in which cattlehides are processed is shown below:

Subcategory	Unhairing	Tanning	Range in Water Use l/kg of hide (gal/lb of hide)
1	Pulp	Chrome	7-156 (0.8-18.7)
2	Save	Chrome	1-189 (0.1-22.6)
3	Save	Vegetable	7-106 (0.8-12.7)

If equivalent leather quality is being produced in each subcategory and with a reasonable allowance for process differences, the variation in

water use seems unnecessarily large. It would appear logical that tanneries with large water use could implement some reduction measures.

Although reduction would result in some savings in water cost, the major saving would result from lower treatment costs. Most unit operations in the treatment process are designed totally or partially on the basis of flow. Therefore, a reduction in flow would reduce both treatment plant capital and operation costs.

Realizing the economy of reduced waste water flows, many tanneries have attempted to decrease water use as much as possible. Some water conservation practices have been implemented and have proven to provide equal or better quality leather than produced previously.

Some methods of water conservation are listed below:

1. Encouraging employees to implement any potential water saving practices. Eliminating the constantly running hoses observed in many tanneries is one practice requiring employee participation.

2. Examine tanning formulas to determine if floats can be reduced. Use of hide processors has permitted use of lower floats.

3. Limit or eliminate some washing and rinsing operations.

   a. Change a continuous rinse to a batch rinse.

   b. Use preset meters or timers to limit total flow.

4. Use of wash waters and rinses for process solution make-up.

Tannery #1 has recently undertaken a comprehensive water conservation program. Through implementation of this program, total water use has been reduced by nearly 50 percent. Installation of hide processors for washing the incoming hides has reduced water use in this process 70 percent. By reuse of process water in the liming operations, a savings of 25 percent has been accomplished. Installation of paddle vats and a recirculating flume arrangement following the unhairing operation has reduced water use for washing 80 percent. Further savings have resulted from recirculating of hair wash water by installing a fine screen for solids removal. Through the installation of a vegetable tannin recycle and reclaim system using evaporators, water use for this process has been reduced 65 percent. The results of such major water conservation measures indicate that a comprehensive water conservation program can substantially reduce water use.

In recent years the hide processor (concrete mixer) has proven to be an extremely effective means of reducing water use. The number of hide

processors in use is increasing. They are most widely used for washing the incoming hides and for beamhouse operations in pulp hair processes.

When hide processors are used in the beamhouse operation, the water use through deliming will be about 8.35 l/kg of hide (1 gal/ lb of hide). Tannery #2, which uses hide processors for all operations from the raw product through chrome tanning or "blue" stage has indicated that water use is from 12.5 to 16.7 l/kg of hide (1.5 to 2.0 gal/lb of hide). Some tanneries have indicated that hide processors are used in the retan, color, and fatliquor operations.

There are also reports of water used in one process being reused in completely separate processes. Tannery #3 uses the same water for washing following their "modified pickle" operation and their vegetable tanning operation. Tannery #1 uses a similar process for recycling the soak water following the vegetable tanning operation back to the color operation that precedes vegetable tanning. There are also some indications that spent liquors previously used in vegetable tanning are reused in retan operations. Tannery #4 indicates that they are using bate waste water for alum tanning make-up water. Tannery #5 is planning to recirculate approximately 20,000 gallons per day of treatment plant final effluent water for use in the delime wash water following the pulp hair process and for wash water following the bate process.

Reuse or reduction of process solutions or recovery of process chemicals has been demonstrated to be a method of waste constituent reduction. A detailed summary of methods available to reduce waste constituents by process adjustments is given by Williams-Wynn (9).

There are a number of vegetable tanneries that are using recycle systems to reduce the amount of tan liquor that is discharged into the waste stream. Although these are not total recycle systems, they do substantially reduce the amount of tanning in the waste stream. In most cases, some blowdown is necessary to prevent the build-up of contaminants in the tanning solution. One tannery recovers this blowdown tan liquor and concentrates it in a triple effect evaporator and sells the concentrated liquor. Other tanneries use this blowdown liquor in retanning operations.

Reuse or recovery of chrome tan liquors is being practiced, but not to the same extent as vegetable tanning solutions. Hauck (6) has presented a summary of methods for recovery and reuse of spent chrome tanning solutions. During World War II, the reuse of chrome tan liquor was common practice because of the scarcity of chromium salts. A recent report by the U.S. Geological Survey states that the country has only "scant reserves" of chromium.

Tannery #6 has performed a study on the reuse of chrome tanning solutions. These tests showed that the chrome liquors could be reused for periods up to six weeks without reduction of leather quality. The

spent tan liquor in this study was settled and sludge was drawn off the bottom of the holding tank. The clarified solution was brought to the required concentration with chromium salts, sulfuric acid, and sodium chloride. Because of the sludge drawoff, this was not a complete recycle systems, however, a substantial portion was recycled and only a small amount wasted.

Tannery #6 also, in this same study, examined the feasibility of recycling of the unhairing solutions. Tests on recycling of the unhairing solutions were performed on three separate occasions. The longest recycle time was two weeks. However, the study concluded that since the concentration of waste material in the solution leveled off after a few days, the solution could conceiveably be reused indefinitely. The spent liquor was drained and settled much in the same manner as the chrome tan liquor. After removing the sludge from the bottom of the tank, 65 percent of the original volume remained. About 50 percent of the sulfhydrate and lime needed for the next run was available in that portion retained for reuse. After two weeks of use, the solution had no objectionable odor and the amount of ammonia coming off was not considered substantial.

Tannery #7 a shearling tannery, has been able to reuse their chrome tan solution up to 5 times. Because of processing requirements, spent chrome tan liquors are not at present being reused.

This same tannery has been able to reuse their pickle liquor up to five times. This is accomplished by adding additional chemicals prior to adding another load of hides.

Tannery #8 reports reusing retan liquors. Tannery #9, reports reusing the finishing oils. Many tanneries are reporting recycling their pasting frame water either wholly or partially.

Based on the above, there are numerous possibilities for process solution reuse. Of particular importance is reuse of the chrome tan solution. If this waste stream enters the total plant waste flow, it will be partially removed in the primary settling tanks when beamhouse wastes or added alkali increases the pH to at least 9.0. This chromic hydroxide precipitate will be removed with the sludge. An additional quantity of chromium will be removed in secondary treatment with possibly some small quantity remaining in the effluent. In order to minimize the chromium content of the sludge and subsequent treatment process, it is proposed that all chrome tanneries be provided with recycle or recovery facilities.

Sulfides in the beamhouse waste constitute a potential problem in subsequent handling. If mixed with wastes which can reduce the pH of the sulfide bearing wastes, hydrogen sulfide is released.

The complete removal of sulfides is ineffective with either plain sedimentation or chemical treatment. Sulfides are more satisfactorily removed through oxidation. Various methods for oxidizing sulfides include:

1. Air oxidation.

2. Direct chemical oxidation (8).

3. Catalytic air oxidation (7) (8) (22).

Air oxidation with diffusers provides some removal, but only with excessive aeration times.

Direct chemical oxidation with ammonium persulfate and ozone were studied by Eye (8). Ammonium persulfate produced low removals. Ozone was most effective; however, the expense of ozone generating facilities and developing contact equipment negated further study (8).

Studies by Chen (22) reveal that many metallic salts are effective catalysts when compressed air at high temperatures is utilized. Manganous sulfate proved to be the most effective catalyst in the more alkaline solutions at near ambient temperatures. Bailey (7) and Eye (8) further describe the effectiveness of the metallic catalysts. In a laboratory study (8), potassium permanganate was the most effective agent, with manganous sulfate also proving effective. Although the relative costs for the two catalysts favor manganous sulfate, the space available and capital costs for the two different systems will determine which catalyst is best for a given situation. Optimum results were obtained with a manganese to sulfide weight ratio of 0.15. Pretreatment facilities employing catalytic oxidation should approach 100 percent removal of sulfides.

Sulfides are also removed in the activated sludge process.

In order to minimize dangers of potential hydrogen sulfide release and to eliminate the BOD exerted in subsequent biological processes, a catalytic oxidation tank is proposed for all tanneries with sulfide bearing wastes.

Preliminary Treatment

Preliminary treatment is defined as those operations performed on the waste stream to make it suitable for introduction into another waste system for further treatment. Normally, the waste system which receives the pretreated waste is that of a municipality or a metropolitan sanitary district, however, it may be subsequent treatment units on-site.

The need for preliminary treatment is based on the following factors:

1. Sewer safety and maintenance.

2. Biological treatment protection.

3. Effluent criteria.

4. Sludge disposal criteria.

Sewerage systems are particularly susceptible to damage from high sulfide wastes. Tannery effluents may contain sulfide concentrations as high as 250 mg/l. An alkaline sulfide bearing waste from a tannery when mixed with sufficient domestic or acidic industrial waste will release hydrogen sulfide gas. At a pH of 7.5, about 30 percent of the sulfide ion in the waste is present as hydrogen sulfide gas. Oxidation of hydrogen sulfide by aerobic bacteria creates sulfuric acid which is corrosive to concrete and metal. This is the major cause of sewer pipe "crown" corrosion. A safety problem for maintenance personnel also develops when hydrogen sulfide gas collects in sewers and manholes due to extreme toxicity in low concentrations. Hydrogen sulfide will also discolor some painted surfaces.

Tannery effluents exhibit a wide range in suspended solids concentrations (300-14,000 mg/l) with an expected average of 2,000 to 3,000 mg/l (10) (11). Grease concentrations in tannery waste can be as high as 850 mg/l.

In addition to added removal problems in a secondary treatment plant, grease can coat sewer lines and act as an adhesive for other particulate matter. The suspended material consisting of much lime may reduce sewer capacity through direct sedimentation. A calcium carbonate scale will form when sufficient carbon dioxide is present.

Aerobic biological treatment processes can be seriously inhibited by some tannery waste constituents. While normal average concentrations of lime and chromium salts do not appear to damage the system, short term high concentrations could be detrimental to biological activity. The high alkalinity (and corresponding high pH) are caused by lime discharges from beamhouse operations. Such discharges are normally intermittent. Trivalent chrome is used extensively as a tanning agent. Hexavalent chrome may appear in trace amounts from some finishing operations, but trivalent chromium is the predominant form in the waste. There appears to be some evidence to indicate that both forms can be toxic (12). Of prime importance is the solubility. Trivalent chromium salts are soluble in acid and neutral solutions. At a pH greater than 8.5, trivalent chromium will be precipitated while hexavalent chromium must be reduced prior to precipitation. Total chromium concentrations of 10 mg/l are indicated as hardly toxic to biological units (13).

The batch nature of tannery operations create wide fluctuations in waste flows and waste strength. Such variance can be difficult to handle, particularly on the conventional smaller treatment plants. The BOD_5 may be as low as 150 mg/l or may exceed 3,000 mg/l with an average usually from 1,000 to 2,000 mg/l (10) (11). Significant reductions in BOD_5 and equalization of flow and waste strength may be required to avert overloading of biological units.

Preliminary treatment operations consist of one or combinations of the following:

1. Screening.

2. Equalization.

3. Plain sedimentation.

4. Chemical treatment.

   a. Coagulation and sedimentation.

      1) Alum.

      2) Lime.

      3) Iron salts.

      4) Polymers.

   b. Carbonation.

5. pH adjustment.

6. Sludge handling and disposal.

These same unit operations and unit processes are used in the first stages of facilities providing a greater degree of treatment required when the effluent is directly discharged to a river or lake.

Screening - Fine screening removes hair particles, wool, fleshings, and hide trimmings. While eliminating undesirable waste water constituents, the screenings themselves create a solid waste disposal problem. The highly putrescible wastes are commonly disposed of on-site or at remote landfill operations. Screening equipment includes coarse screens (bar screens) and fine screens, either permanently mounted or rotating with self-cleaning mechanisms. The exact contribution of screenings on parameters such as BOD_5 and suspended solids is not known, since large particles are removed prior to obtaining samples for testing. The principal function of screening is to remove objectionable material

which has a potential for damaging plant equipment and clogging pumps or sewers.

Equalization - Equalization of waste streams is important in pre-treatment facilities. The volume and strength of waste liquors vary depending on process formulations and scheduling of tannery operations. Alkaline wastes are associated with beamhouse operations, while acid discharges occur from the tanyard. In order to produce optimum results in subsequent treatment operations, equalization of flow, strength, and pH of strong liquors is required. Although some oxidation may occur, no removal of waste constituents is normally reported for equalization. Equalization basins provide storage capacity for hydraulic balance. Auxiliary equipment must provide for mixing and maintaining aerobic conditions. Detention times much less than one day are usually provided. Basins can be monitored through pH and flow measurement.

Plain Sedimentation - Plain sedimentation is concerned with the removal of non-flocculating discrete particles and floatable low density materials such as grease and scum. Tannery wastes have high concentrations of both suspended solids and grease. As shown in Table 8, suspended solids reductions can range from approximately 40 to 90 percent, while reductions in BOD_5 can range from 30 to 60 percent. Much of the suspended material removed is in the form of insoluble lime which produces a voluminous and heavy sludge. Although grease removals are not indicated, high removals are expected with surface skimmers installed in clarifiers.

TABLE 8

PLAIN SEDIMENTATION

System	Suspended Solids Inf. mg/l	Suspended Solids Eff. mg/l	Suspended Solids Removal %	BOD Inf. mg/l	BOD Eff. mg/l	BOD Removal %	Remarks	Reference
Lagoon	---	---	80-90	---	---	80-90	Fill and draw basins with 24-hour capacity.	(38) (39)
Sedimentation tanks, mechanical sludge facilities	900	130	83-88	380	146	40-63	Pretreatment of vegetable tan liquors. Detention time 9-15 hours.	(40)
Sedimentation tanks	1,200	370	69	---	---	---	Detention time 2 hours	(14)
Sedimentation tanks	1,184	680	43	1,046	537	48	Continuous flow (pilot)	(41)
Sedimentation tanks	1,880	461	67	1,285	873	30	Fill and draw (pilot)	(41)

Assumed to be typical for plain sedimentation units is the full-scale operation cited by Sutherland (14). The suspended solids content of a side leather tannery was reduced 69 percent from 1,200 mg/l to 370 mg/l by continuous flow sedimentation for two hours.

Laboratory experiments by Sproul, et al., (15) utilizing beamhouse and chrome liquors showed that plain sedimentation at an overflow rate of 24.5 cu m/day/sq m (600 gpd/sq ft) gave average removals of about 22 percent in suspended solids and 35 percent in BOD. Pilot scale experiments by Sproul, et al., (51) show equalization of plant flows followed by plain sedimentation gave suspended solids and BOD removals up to 99 and 50 percent, respectively. Chrome liquors in excess of 1 percent of the total flow proved to be an effective coagulant for composite wastes containing 2,000 mg/l suspended solids. Overflow rates of 14.3 cu m/day/sq m (350 gpd/sq ft) produced a 2 percent underflow concentration.

Field observations at Tannery #10 tend to confirm these removals. The primary units consist of two circular clarifiers with overflow rates of 18.8 cu m/day/ sq m (460 gpd/sq ft) at an average flow of 3,030 cu m/day (0.8 mgd). No equalization facilities are provided other than mixing in a pump wet well. Cattlehide processing during the sampling period averaged 81,700 kg (180,000 lb) green salted hides per day for pulp hair house operations followed by chrome tan and finishing. The following average removals resulted (10).

	Influent mg/l	Effluent mg/l	% Removal
Suspended Solids	3,125	945	70
BOD_5	2,108	1,150	45
Total Chromium	51	24	53
Total Alkalinity (as $CaCO_3$)	980	718	27
Grease	490	57	90

Suspended solids and BOD_5 removals were 70 percent and 45 percent, respectively. A low chromium removal of approximately 50 percent occurred. Higher removals would result if a pH of 8.5 or greater were maintained (using equalization or chemical addition) in the primary clarifiers. If sodium alkali is contributing to the high pH, a pH of 10-10.5 may be needed for best removal. Theoretically, all chrome should precipitate as chromic hydroxide; however, a very small residual is expected. Although chrome removal from the waste water is desirable, a sludge problem is created if proper disposal precautions are not taken. The total alkalinity was reduced 27 percent, reflecting sedimentation of suspended lime. Grease removal was 90 percent.

In general, plain sedimentation is a physical separation of some suspended particles from the waste stream. Although high removals of suspended solids (90 percent) and BOD (60 percent) are indicated with equalization and sedimentation, effluent concentrations are not reported below 130 mg/l for suspended solids or 146 mg/l for BOD_5 (Table 8). High chromium removals may result while sulfide concentrations are relatively unaffected. As a unit operation, plain sedimentation has desirable application in tannery waste water treatment.

Chemical Treatment - Coagulation and Sedimentation - Chemical addition prior to sedimentation has further increased the removal efficiencies of primary clarifiers. Chemical coagulation results in higher removals of suspended solids, BOD, sulfides, chrome, and alkalinity through flocculation of colloidal particles. Alum, lime, iron salts, and polymers have exhibited satisfactory results. Data in Table 9 indicates that suspended solids removals from 50 to above 95 percent and BOD_5 reductions range from approximately 50 to 90 percent are achieved.

Chemical coagulation followed by sedimentation has been investigated by Sproul, et al. (15) at a cattlehide tannery using the chrome process. Raw waste water analyses indicate concentrations of BOD_5 at 2,500 mg/l and suspended solids of about 2,530 mg/l. The results drawn from the laboratory scale investigation are shown in Table 9 (15).

1. Use of an anionic polymer at a concentration of 1 mg/l resulted in a reduction of about 84 percent in suspended solids and 60 percent in BOD_5.

2. Adjustment of the waste to pH 9.0 with sulfuric acid and subsequent settling gave average removals for suspended solids and BOD_5 of 90 and 67 percent, respectively.

3. Use of ferric chloride at a concentration of 600 mg/l produced average removals of 60 to 65 percent, respectively, for suspended solids and BOD_5.

4. Ferric chloride coagulation was less effective in removal of suspended solids than was adjustment to the same pH with sulfuric acid.

5. Coagulation with alum at concentrations less than 500 mg/l after adjusting to a pH of 6.5 reduced the BOD_5 by 90 percent and suspended solids from 45 to 57 percent. Alum concentrations higher than 500 mg/l created a floc that would not settle.

6. Buffing dust resulting from finishing tanned hides was not found to be an effective coagulant.

TABLE 9

CHEMICAL TREATMENT

System	Coagulants	Suspended Solids Inf. mg/l	Suspended Solids Eff. mg/l	Suspended Solids Removal %	BOD Inf. mg/l	BOD Eff. mg/l	BOD Removal %	Remarks	Reference
Coagulation-Sedimentation									
Plain Sedimentation, Coagulation, Sedimentation	Alum	1,550	68	96	--	--	90*	Adjustment of pH water H_2SO_4	(42)
Aeration, Coagulation, Sedimentation	Alum	2,500	850	66	3,800	1,030	73	A pilot study with presettling of a portion of the raw waste with adjustment of pH to 5.5. Mixing aerated raw waste with presettled supernatant indicated 93% color removal.	(18)
Coagulation, Sedimentation	Lime	918	469	49	1,001	476	52	Continuous flow with lime concentrations of 1,490 mg/l.	(41)
Coagulation, Sedimentation	Lime	1,980	497	75	1,630	823	49	Fill and draw with lime concentrations of 1,700 mg/l.	(41)
Coagulation, Sedimentation	Lime	3,135	110	95	1,437	619	57	Adjustment of pH with beamhouse liquors. Overflow rate, 25.9 cu m/day/sq m (635 gal/day/sq ft)	(37)
Coagulation, Sedimentation	Iron Salts			High			High	Ferric chloride added at concentrations of 2,000-5,000 mg/l	(16)
Coagulation, Sedimentation	Polymer	5,200**	500**	90	--	--	--	Full-scale operation on beamhouse wastes with anionic polymer addition of 10 mg/l. Overflow rates at 65 cu m/day/sq m (1,600 gpd/sq ft)	(32)
Carbonation									
Equalization, 2-stage Carbonation, Coagulation, Sedimentation	Lime	--	--	--	13,400	1,140	92	A pilot study with equalization of flow, carbonation with flue gas to 6.4-6.7 pH. Coagulation with lime followed by 3-hour sedimentation. Effluent is then subjected to a second stage process similar to the first. A 99% reduction in color resulted.	(19)
Carbonation, Coagulation, Sedimentation	Iron Salts	6,190	58	99	2,180	325	85	A pilot study with carbonation of beamhouse wastes to a pH of 6.0 followed by coagulation with ferric chloride (300-500 mg/l). Treatment produced a floc which settled quickly.	(19)

* Oxygen demand.
** Order-of-magnitude values

In general, polymer addition produced a rapid formation of floc minimizing the need for flocculating equipment. Without pH adjustment, polymers produced consistently higher removals than other coagulants tested.

Sulfides appearing in the primary influent are not completely removed in chemical units. Inconsistent removals are indicated in the literature by researchers (8) (16) (17). With pH adjustment to 8.0, an upper limit on sulfide removal may be 90 percent (15). Sulfide removal reduces BOD_5 and averts hydrogen sulfide problems.

Chromium will precipitate as a hydroxide at a pH greater than 8.5. A 90 percent removal in a laboratory study by Sproul, et al. (15) occurred at a pH of 8.0. Precipitation in a primary sedimentation unit is desirable to prevent any potential toxicity in subsequent biological treatment units.

The removal of color is not commonly reported by investigators. Low removals are, therefore, expected. In pilot plant operations described by Howalt and Cavett (18) and also by Riffenburg and Allison (19), 93 and 99 percent removals of color were observed, respectively. The exact mechanism of removal in each of these studies is not indicated. However, since color exists in the colloidal region, a physical-chemical process is implied.

In a thesis by Hagan (20), color removal through coagulation and precipitation was investigated. In coagulation, inter-particle attraction created by suitable polymers develops a large floc that tends to settle at an optimum pH. Hagan also reported that common ion effect assisted in precipitation removal. The basis of this contention is that the high hydroxyl ion concentration at high pH reduces the solubility of color vectors such as digallic acid which contains hydroxyl functional groups. Addition of coagulants and pH control at this point may further increase the relative efficiency. Laboratory results on a vegetable tannery waste indicate high color removals (94 percent) through a combination of chemical precipitation and coagulation with calcium hydroxide and an anionic polymer (20). The efficiency is dependent on pH control around 12.

In general, constituent reductions with coagulants are limited to suspended solids, chromium, and possibly sulfide and color. BOD_5 removals are a function of that portion of the BOD_5 existing in the colloidal or suspended form. Soluble BOD_5 is normally 40 to 50 percent of the total BOD (10). Many low removal efficiencies may have resulted from inefficient control of the physical-chemical operations, which require operator attention to be successful.

<u>Chemical Treatment - Carbonation</u> - Carbonation is effective in the treatment of alkaline wastes. In this process, carbon dioxide reacts with lime to form calcium carbonate, which has a solubility of only 25

to 50 mg/l. The crystalline structure of the carbonate nucleus provides an effective surface for adsorption of organic matter. Suspended solids and BOD are both reduced.

Stack gas containing 8 to 12 percent carbon dioxide obtained from any fuel combustion process can be used. Introduction of gas into the waste stream requires a suitable diffuser system and reaction vessel.

Table 9 indicates high removals for suspended solids, BOD_5, and alkalinity for carbonation in conjunction with coagulation. The BOD_5 removals range from 85 to 92 percent, while suspended solids reductions as high as 99 percent are recorded.

Field data from Tannery #3 indicate high reductions in suspended solids, BOD, and total alkalinity. Estimated flows from the cattlehide vegetable tannery were 1,700 cu m/day (0.45 mg/l). Primary clarifier overflow rates were about 20.4 cu m/day/sq m (500 gpd/sq ft) for a chemical system utilizing flue gas carbonation and a combination of iron salts and polymers. (Sulfuric acid is also used to assist pH control). The following removals were indicated (21):

	Primary Influent mg/l	Primary Effluent mg/l	% Removal
Suspended Solids	2,110	100	95
BOD_5	1,660	270	84
Total Alkalinity (as $CaCO_3$)	640	0	100

Carbonation is attractive for tannery pretreatment facilities, since in most cases carbon dioxide is available at the cost of piping from the plant boilers. Removals are high, under proper operating conditions, for suspended solids and BOD.

pH Adjustment - In some instances, pH correction of the waste effluent from other pretreatment processes has been required to meet restrictions of a receiving system. Normally this has been accomplished by feeding sulfuric acid or sodium hydroxide to lower or increase pH as required. This requires a relatively simple chemical feeding equipment with pH sensing and control system.

Sludge Handling and Disposal - A major part of tannery waste treatment is handling and disposal of the semi-solid sludges obtained from liquid treatment processes. The most predominate methods of ultimate disposal of tannery waste sludges includes sludge lagoons, landfills, dumps, and spreading on the land.

Some attempts have been made to dewater sludges prior to ultimate disposal with varying success. The three principal dewatering techniques include centrifuges, vacuum filters, and pressure filtration. The centrifuges have appeared to meet with less success than vacuum filters or pressure filters.

Stabilization of sludges prior to disposal using aerobic and anaerobic digestion has not been used extensively and where it has been tried, it has not always been extremely successful. Some of the organic matter is difficult to decompose by biological activity and probably is the reason for at least a part of the difficulties associated with digestion. In addition, high chromium levels can inhibit the activity of some microorganisms which stabilize organic material.

Reducing the moisture content of sludge by spreading on drying beds has also been successful in some areas. This is particularly attractive to smaller facilities where land area is available.

Conditioning and stabilizing a mixed domestic and tannery sludge using heat treatment processes has been employed also at Tannery #11 (about 80 percent of the waste flow is tannery waste). Such heat treatment provides a stable end product from a biological standpoint and can be incorporated in a landfill or spread on the land. One of the principal difficulties with tannery waste is the chromium content in sludges and the potential impact this material has on the environment from a toxic standpoint. In testing a heat treated sludge, it has been indicated that some of the trivalent chromium may be oxidized to the hexavalent form. Apparently, the trivalent chromium is converted through the high temperature, high pressure, and oxidizing environment of the heat treatment process.

When chromium is reused in the tannery, levels in the sludge are reduced. Disposal of sludge containing these residual quantities of chromium in a sanitary landfill will minimize any environmental problems.

Prior to dewatering in mechanical equipment, sludge is normally conditioned by use of ferric salts and lime or polymers or a combination of these. The quantity and type of chemicals required are dependent upon characteristics of the sludge being handled.

Dewatering with mechanical equipment generally can produce a solid cake containing 15 to 30 percent solids.

Some sludge is disposed of on the land taking advantage of its lime content for agricultural purposes. One disadvantage of this type of disposal practice is the potential toxic effects which chromium or other constituents might have on plants or through leaching to ground or surface water supplies.

Lagoons for dewatering have some limited uses. In humid areas where evaporation approximates rainfall, such application is not completely satisfactory.

Use of lagoons, drying beds, landfills, and landspreading all require key attention to the environmental impact. Particularly important is the leaching of potential toxic or organic materials on the ground water supplies or surface waters. Proper controls must be taken to ensure that these conditions will not develop.

Spreading tannery sludge on the land may also be a potential problem from the standpoint of bacteria present. However, with the high amount of lime waste commonly found in most tannery sludges, as well as the lime dosages required prior to dewatering, there is usually sufficient contact time of the sludge at a high pH to afford some degree of disinfection. In most cases, it is desirable to have the sludge elevated to a pH of about 11.5 or greater for about two hours or more to effect proper control.

Preliminary Treatment - Facility Requirements - Based on an appraisal of needs and the performance of previously described operating facilities, the following processes are included in evaluating preliminary treatment requirements:

Waste Flow

Screening
Equalization
Primary settling

Sludge

Collection
Thickening

Provision is also included for chemical addition to the primary settling tank to aid in clarification and sludge settling.

Adequate experience has been accumulated to ensure that facilities will perform satisfactorily. However, in some installations, attempts have been made to combine equalization and settling in one unit. In some instances, a large settling tank has been utilized to perform this function. The success of such an approach depends on a waste dump program. In theory, continual vigorous mixing required for rapid equalization is not compatible with the essential quiescent condition desirable for efficient settling. Initial screening of the waste is desirable to remove large particles prior to further treatment.

Secondary Biolcgical Treatment

Parameters used for sizing principal items of equipment are as follows:

Equalization	Detention:	24 hours at design flow
Primary Settling	Overflow rate:	23.5 cu m day/sq m (500 gpd/sq ft)
Waste Sludge	2 percent solids	
Vacuum Filter	Loading rate:	15.6 kg/sq m/hr (3.2 lb/sq ft/hr)

Major Reduction of BOD5 and Suspended Solids - Major reduction of BOD5 and suspended solids requires a higher degree of treatment than that provided by normal primary or preliminary treatment facilities. This higher level of treatment is referred to as secondary biological treatment. It generally includes a biological unit process and may or may not require a pretreatment step. Such facilities may be located at a municipal plant treating a combined municipal-tannery waste or may be an on-site plant treating only tannery wastes. Secondary biological treatment can utilize activated sludge, lagoons, or trickling filters along with required supporting equipment to achieve required effluent quality. All systems with sufficient design capabilities and adequate operation can attain equivalent efficiency of BOD5 and suspended sclids removal. Numerous biological treatment schemes are, therefore, feasible. Selection of an alternative biolcgical treatment system is influenced by waste water constituents, required efficiencies, climatic conditions, land requirements, operational characteristics, and economics.

Combined Municipal-Tannery Treatment Systems - Combined treatment of tannery and municipal waste waters predominates in the industry since most tanneries are located in urban communities (4). Such systems normally require some degree of pretreatment at the tannery. Typically, tannery effluents are combined in various proportions with domestic flows and subjected to treatment by activated sludge or trickling filter systems. Other combined treatment facilities such as lagoons are not commonly reported. Shown in Table 10 are reported combined municipal-tannery treatment efficiencies. One example of primary treatment only has been included to serve as basis of comparison with secondary biological treatment systems.

TABLE 10

COMBINED MUNICIPAL-TANNERY TREATMENT SYSTEMS

Systems	Tannery Pretreatment	Total Flow cu m/day (mgd)	Tannery Flow %	BOD_5 Inf. mg/l	BOD_5 Eff. mg/l	BOD_5 Removal %	Suspended Solids Inf. mg/l	Suspended Solids Eff. mg/l	Suspended Solids Removal %	Location	Remarks	Reference
Primary												
Pre-aeration, sedimentation, chlorination, vacuum filtration	Holding tank	2,195 (0.58)	35	326	156	52	883	760	15	Williamsport, Pennsylvania	Low removals are a result of a chemical reaction between sewage, tannery waste, and filtrate from vacuum filters.	(44)
Trickling Filter												
Trickling filter			15			90			90			(45)
Trickling filter	Carbonation, sedimentation		40	600	65	89				Lawrence Engineering Experiment Station	Removal obtained with loadings of 1.3-1.7 kg BOD_5/day/cu m (3,500-4,500 lb BOD_5/day/ac ft). No scale deposition on media. 100% sulfide removal.	(46)
Trickling filter, sludge digestion	Screening	35,958 (9.5)	14			87			86	Sheboygan, Wisconsin	Before initiating screening experienced problems with hair and hide scraps in digester.	(47)
Trickling filter, sludge digestion, sludge lagoon	Screening, grease removal	24,224 (6.4)	47	340		63	1,068		79	Fondulac, Wisconsin	Vacuum filtration and incineration discontinued due to lack of efficiency.	(47)
Trickling filter, sludge drying beds		14,383 (3.8)		510		58-60	630			Gloversville, New York	Present facility is operating at double the design capacity with obsolete settling basins.	(47)
Activated Sludge												
Activated sludge, separate sludge digestion, land irrigation of liquid sludge	Sedimentation	4,542 (1.2)	14		>100	95		>100	90	Aurora, Ontario, Canada	Theoretical aeration detention times for each basin are 7 hours.	(47) (48)
Activated sludge, separate sludge digestion, land irrigation of liquid sludge	Screening with potential of sedimentation units	6,056 (1.6)	37	360			800			Barrie, Ontario, Canada	Plant completed in 1965 with capacity of 13,626 cu m/day (3.6 mgd).	(47)
Activated sludge, separate sludge digestion	Lagoon	14,383 (3.8)	4	175	18	90				Columbus, Indiana	Tannery out of operation since 1962. Treatment plant experienced operational problems with comminutors, diffusers, and digesters.	(47)
Activated sludge, sludge dewatering by centrifugation, land disposal	Equalization, sedimentation, carbonation	(Variable)	45		32	90		200	75	South Paris, Maine	Pilot operation.	(23)
Other												
Bio-filtration 2-stage oxidation pond, separate sludge digestion, lagoon sludge disposal		16,276 (4.3)	6	242	9	96	325	31	90	Napa, California	Flow from two tanneries. Chrome reduced from 6.1 to 0.8 mg/l. Digester gas 0.585 cu m/kg (9.5 cu ft/lb) volatile matter added.	(47)
Primary sedimentation, roughing filter, activated sludge, secondary sedimentation		1,514 (0.4)				82-99			66-78	Gloversville, New York	Prototype operation, visual indication of highly effective color removal.	(24)

All treatment methods have demonstrated capability in at least one installation to remove 90 percent of BOD_5 and suspended solids. However, other installations using the same treatment methods have not achieved this degree of treatment. Tannery flow combined with domestic sewage has ranged from less than 5 percent to more than 80 percent of the total. Studies of combined treatment by Camp, Dresser, and McKee (23) and Nemerow and Armstrong (24) present typical applications of this approach.

In a pilot study for a tannery in the Northeast (#12), appropriate design parameters for combined treatment of tannery with domestic sewage was investigated. Approximately equal portions of tannery and domestic sewage were used. Test flows ranged from 0.3-1.3 l/sec (5-20 gpm). At the time of the study, the tannery production was approximately 1,502,740 kg (3,310,000 lb) of cattle hides per month with an estimated waste water flow of 3,785 cu m/day (1 mgd) from beamhouse, chrome tan, and finishing processes. Combined flows consisting of equal portions of tannery and municipal effluent totaling 9,463 cu m/day (2.5 mgd) are proposed for the full- scale facility. Removals in excess of 90 percent BOD_5 and suspended solids were required to meet stream classification standards. The following full-scale unit processes, listed in the order of application, were found to be essential to meet requirements (23).

1. Equalization.

2. Primary sedimentation.

3. Carbonation and sedimentation.

4. Addition of municipal sewage.

5. Activated sludge treatment.

6. Sludge dewatering by centrifuge.

7. Effluent chlorination.

Equalization, carbonation with flue gasses, and sedimentation are proposed as a pretreatment for tannery wastes.

Equalization is an important unit process for minimizing variations in discharge flows and waste strength. Based on the quantity and quality of the tannery discharge, a minimum of 4 hours was found to provide sufficient equalization capacity.

Primary sedimentation basins designed with an overflow rate of 32.9 cu m/day/sq m (700 gpd/sq ft) should produce a sludge with 8 percent solids. Heavy duty sludge removal equipment will be required due to the volume and density of the sludge produced.

Pilot tests indicate that carbonation after equalization provides a rapid absorption of carbon dioxide (CO_2) gas. A contact time of 20 minutes was sufficient for flue gas carbonation. The resulting calcium carbonate precipitate is expected to aid in the removal of other suspended solids by sedimentation prior to secondary treatment.

A volumetric loading of about 973 kg BOD_5/day/1,000 cu m (60 lb BOD_5/day/1,000 cu ft) for the aeration basin with aeration capacity of 123 kw (165 hp) is proposed for combined treatment. Tests indicate foaming may be an operational problem. The full-scale design should include provisions for surface sprays and chemical addition.

The biological floc produced in the pilot aeration basin was very light and settled with difficulty. An overflow rate not to exceed 23.5 cu m/day/sq m (500 gpd/sq ft) is proposed for secondary sedimentation. Upon resettling of the waste secondary sludge in the primary clarifier, a mixture resulted which dewatered readily on drying beds. Since large volumes of sludge are produced, excessive amounts of land would be required for drying beds. Sludge is, therefore, proposed to be dewatered in a solid bowl centrifuge with the resulting cake containing 20 to 30 percent solids hauled to a sanitary landfill.

Nemerow and Armstrong (24) investigated a two-stage biological system. A prototype plant treated 1,514 cu m/day (0.4 mgd) flow intercepted from a combined municipal and tannery sewerage system. The exact proportions of each were not indicated. The treatment system consisted of the following processes:

1. Primary sedimentation.

2. Roughing filter.

3. Activated sludge.

4. Secondary sedimentation.

The primary sedimentation unit with overflows between 15.5 and 23.0 cu m/day/sq m (330 and 490 gpd/sq ft) produced removal efficiencies of 48 percent for BOD_5 and 24 percent for suspended solids. Comparable values with polymers were 75 percent and 39 percent, respectively (24). The organic load on the filter ranged from 1,135 to 3,242 kg BOD_5/day/1,000 cu m (70 to 200 lb BOD_5/day/1,000 cu ft) with BOD_5 removals of 37 and 30 percent, respectively (24). The activated sludge unit produced the highest organic removal efficiency (85 percent) at food to active mass (F/M) ratio of 0.2. The mixed liquor suspended solids (MLSS) concentrations in the parallel basins were maintained at 2,000-3,500 mg/l. Flotation thickeners without polymers were loaded at 5.9 to 17.1 kg/sq m/hr (1.2 to 3.5 lb/sq ft/hr) and consistently produced sludge concentrations of 5 percent. Total system BOD_5 removals ranged between 80 to 90 percent.

In general, combined treatment is viable if proper design considerations assessing the effects of tannery waste waters are considered.

High treatment efficiencies are technically possible in all processes. Combined treatment usually requires that certain restrictions be imposed by the municipality on waste water constituents, including chrome, sulfides, alkalinity, grease, pH, and in some instances BOD_5 and suspended solids.

On-Site Treatment - Trickling Filter Systems - Trickling Filter Systems are not extensively utilized for tannery treatment. Reasonably high efficiencies are technically possible, yet the positive control needed for high strength waste treatment has not been generally demonstrated.

A trickling filter is an aerobic biological unit. Wastewater constituents are brought in contact with microorganism mass developed on the surface of the filter media. To achieve high removals from tannery effluents, toxicity and excessive organic loads must be prevented. Lime deposition on filters has, in some instances, retarded biological activity. Also, the high strength of tannery wastes require that a large surface area be provided. Although recirculation and improvements in filter media may reduce overall area needs, the removal efficiency may not be sufficiently consistent through the warm and cold periods to meet the demands of future effluent requirements. Temperature is critical in operation. High heat losses can result from the spray distribution system and bed media, yielding low efficiencies. Populations of nitrifying organisms are suppressed due to the continual dosing of the system with carbonaceous organic material.

Data is generally limited on trickling filter applications. Presented in Table 11 are reported efficiencies for trickling filter systems. A tannery in the Southeast (#3), utilizes a trickling filter as the first stage in a two-stage biological system. Operational data reported in 1972 indicate the plastic media filter was ineffective with removals of less than 30 percent in BOD_5 and suspended solids (25). After cleaning the media and increasing the air supply to the filter, Kinman (26) reported improvements to the overall system. Confirming data obtained in a recent field survey at Tannery #3 indicate the trickling filter (oxidation tower), including secondary clarification, has the following combined performance characteristics (21):

	Influent to Trickling Filter mg/l	Effluent from Clarifier mg/l	Removal %
BOD5	270	62	78
Suspended Solids	110	45	59
COD	---	240	---
Total Kjeldahl Nitrogen (as N)	---	210	---
Ammonia Nitrogen (as N)	---	61	---
Color	---	300 units	---

The flow to the filter was approximately 3,785 cu m/day (1 mgd), including a 50 percent recycle of the secondary clarifier effluent. The BOD5 and suspended solids were reduced 78 percent and 59 percent, respectively. Considering the low influent concentrations, these removals appear to be satisfactory. Further reduction in BOD5 and suspended solids may not be possible due to the colloidal characteristics of the suspended material and the relatively high overflow rate of 37.6 cu m/day/sq m (800 gpd/sq ft) in the secondary clarifier. Based on estimated influent characteristics, moderate COD removals are expected, with essentially no reduction in nitrogen and color.

Trickling filters have limited application in the treatment of high strength tannery wastes. System upsets are common due to organic overload and climatic conditions. Existing filters may be incorporated into systems for preliminary treatment prior to a second stage biological system.

On-Site Treatment - Aerobic Lagoon Systems - Aerated lagoon systems have been utilized for tannery treatment where land is readily available. Lagoons serve a two-fold purpose, providing equalization and a desirable environment for biological activity. In a large lagoon with proper inlet and outlet control, primary and final sedimentation may be eliminated. An aerobic environment is maintained by mechanical aerators designed with capacities to introduce sufficient oxygen to meet metabolic requirements and to provide adequate mixing. Under variable loadings the usually long detention times have produced reasonably consistent effluent characteristics. Temperature is important because the large surface area permits sizable and latent heat loss to the atmosphere.

Presented in Table 12 are removal efficiencies for those tanneries utilizing aerated lagoons. Although the design potential for high removals is documented, existing operations have not attained high

efficiencies consistently. A reassessment of unit functions and more operative control may be required.

TABLE 11

TRICKLING FILTER SYSTEMS

	BOD_5 Inf. mg/l	BOD_5 Eff. mg/l	BOD_5 Removal %	Remarks	Reference
Carbonation, primary sedimentation, trickling filter, final sedimentation	-	-	85-95	Indicate 100 percent removal of sulfides	(4)
Primary coagulation, sedimentation, trickling filter, final sedimentation	-	30-80	80	Adjustment of pH before primary sedimentation	(27)
Dilution, primary sedimentation, trickling filter, final sedimentation	900	56	94	Foreign data (India). Influent BOD_5 concentration after primary sedimentation	(28)
Dilution, primary sedimentation, trickling filter, final sedimentation	821	48	84	Foreign data chrome tannery (India). Influent BOD_5 concentration after primary sedimentation	(28)

TABLE 12
AEROBIC LAGOON SYSTEMS

System	Total Flow cu m/day (mgd)	BOD_5 Inf. mg/l	BOD_5 Eff. mg/l	BOD_5 Removal %	Suspended Solids Inf. mg/l	Suspended Solids Eff. mg/l	Suspended Solids Removal %	Total Nitrogen Inf. mg/l	Total Nitrogen Eff. mg/l	Total Nitrogen Removal %	Tannery	Process	Remarks	Reference
Screening, plain sedimentation lagoons, aerated lagoons, final sedimentation lagoons	719 (0.19)	1,800	100	95							Middlesboro Tanning Co., Middlesboro, Kentucky	Cattle, save-pulp, chrome-vegetable	Separate screening and sedimentation of tan and beamhouse liquors prior to aeration.	(10)
Sedimentation lagoons, aerated lagoon, final sedimentation lagoon, lagoon sludge disposal	4,580 (1.21)	400	190	53	564	82	86				Armour Leather Co., Bolivar, Tennessee	Cattle, save, chrome	Represents 1-24 hr. composite sample.	(21)
Screening, plain sedimentation, coagulation sedimentation, aerated lagoons	2,309 (0.61)	2,250	815	64	1,500	725	52				Virginia Oak Tannery, Luray, Virginia	Cattle, save-pulp, vegetable-chrome	Employ the lurl-tan process. No effluent vegetable tanning.	(10)
Equalization, plain sedimentation, aerated lagoon, final sedimentation	151 (0.04)	1,750	128			200			100-NH_3		Gunnison Bros., Inc., Girard, Pennsylvania	Cattle, save, vegetable	Segregation of waste streams prior to aeration. Aeration detention time 20 days.	(10)

In a prototype study at a tannery in Virginia (#13), Parker (29) investigated aerobic treatment of vegetable tanning wastes. The system included separate equalization for beamhouse and tanning waste waters prior to mixing with bating flows. Beamhouse wastes were eventually diverted to another facility when pumping problems developed. Mixed tannin and bating wastes were then aerated in a lagoon. The lagoon volume was approximately 2,984 cu m (0.77 mg) with 7.5 kw (10 hp) aeration capacity. Based on average influent data and prorated effluent characteristics, the following removals were observed:

	Influent mg/l	Effluent mg/l	Removal %
BOD_5	1,043	86	92
Suspended Solids	539	571	0
COD	4,470	1,608	64
Sulfide	1.5	0	100
Total Kjeldahl Nitrogen	88	22	75

A relatively high degree of BOD_5 removal (92 percent) resulted at a volumetric loading of 73 kg BOD_5/day/1,000 cu m (4.5 lb BOD_5/day/ 1,000 cu ft). Investigators report the loading may range from 16.2 to 130 kg BOD_5/day/1,000 cu m (1 to 8 lb BOD_5/day/1,000 cu ft) for BOD_5 removals exceeding 80 percent (29) (30) (31).

Effluent temperatures varied between 5°C (41°F) to 8°C (46°F) during winter operation. Sulfides were completely oxidized. The kjeldahl nitrogen removal (75 percent) indicates some nitrification occurred in the lagoon with hydraulic detention times of 16 to 35 days. The "BOD removal factor" ranged from 1.42 day^{-1} to 1.82 day^{-1} for the various operational phases (29).

In general, aerobic lagoons are capable of providing high removals of BOD_5 and sulfides with a potential for some nitrification with long detention periods. Existing facilities need upgrading through proper monitoring and control. The successful application of aerobic systems will be contingent on the availability of land and proper assessment of the climatic factors influencing design.

On-Site Treatment - Aerobic Plus Anaerobic Lagoon Systems - Aerobic plus anaerobic lagoons are finding increasing application in tannery waste treatment. Existing lagoons are easily modified to operate simultaneously in these modes. A stratified lagoon offers the optimum characteristics of both biological functions. The lower anaerobic zone, although requiring an extended contact time, is effective in treating high strength organic wastes. The degradation products produced are:

methane, hydrogen sulfide, and ammonia which are readily available for utilization or further removal. Since the process does not require dissolved oxygen, minimum surface area to volume ratios are required. In general, the anaerobic process produces a waste which is more amenable to subsequent treatment. A more complete degradation occurs in the upper or aerobic zone of the lagoon. The major decomposition products are carbon dioxide and water. Aerobic surface conditions are required to prevent escape of anaerobic products which create odors such as hydrogen sulfide.

Stratified lagoons are generally deep, 3.7-4.6 m (12-15 ft), but shallow depths, 1.2-1.5 m (4-5 ft), are sometimes employed. Mechanical aerators equipped with erosion shields provide the desired surface oxygen requirements without disturbing the lower anaerobic zone.

Presented in Table 13 are data for aerobic-anaerobic lagoons treating tannery effluents. The limited data available indicates some inconsistency in results. A better analysis of the system merits are covered in the studies of Parker (29) and Eye (32).

TABLE 13

AEROBIC-ANAEROBIC SYSTEMS

System	Total Flow cu m/day (mgd)	BOD Inf. mg/l	BOD Eff. mg/l	BOD Removal %	Suspended Solids Inf. mg/l	Suspended Solids Eff. mg/l	Suspended Solids Removal %	Total Nitrogen Inf. mg/l	Total Nitrogen Eff. mg/l	Total Nitrogen Removal %	Tannery	Process	Remarks	Reference
Screening, aerobic-anaerobic 2-stage lagoons	2,271 (0.6)	673	53	92	339	48	86				Pownal Tanning Co., North Pownal, Vermont	Cattle-sheep save, chrome	Nitrification-denitrification is not indicated.	(10)
Screening, plain sedimentation, aerobic-anaerobic lagoon, final sedimentation, chlorination	1,363 (0.36)	2,300	600*	74	3,000	165*	95				Howes Leather Co., Curwensville, Pennsylvania	Cattle, save, vegetable	Primary settling of beamhouse flows prior to mixing with spent tans.	(10)

*Arithmetic average.

An aerobic-anaerobic prototype system was investigated by Parker (29) for treatment of a vegetable tannery waste consisting of bating and vegetable tanning waste flows in a proportion of 8:1. The aeration capacity of 7.5 kw (10 hp) and volume of the lagoon were held constant while flows were varied to impart various loadings on the system. In the initial phase the following removals were experienced:

	Influent mg/l	Effluent mg/l	Removal %
BOD_5	1,170	274	76
Suspended Solids	---	503	---
COD	4,730	2,113	55
Sulfide	0.7	0	100
Total Kjeldahl Nitrogen	107	35	67

The BOD_5 removal was approximately 76 percent for an organic loading of 141 kg BOD_5/day/1,000 cu m (8.7 lb BOD_5/day/1,000 cu ft). Temperatures ranged from 5°C (41°F) to 24°C (76°F) for this operational phase. Suspended solids in the effluent were high, indicating the need for more effective final clarification. Sulfides were completely oxidized in the aerobic zone. The kjeldahl nitrogen removal of 67 percent indicates significant nitrification occurring in the system with hydraulic detention times of 4 to 8 days.

In the second phase of operation, doubling the organic load to 282 kg BOD_5/day/1,000 cu m (17.4 lb BOD_5/day/1,000 cu ft) did not significantly reduce the efficiency. Investigators report loadings of aerobic-anaerobic systems may range from 130 to 243 kg BOD_5/day/ 1,000 cu m (8 to 15 lb BOD_5/day/1,000 cu ft) for 80 percent organic removals (29) (30) (31) (35) (36 (50). However, loadings above 81 kg BOD_5/day/1,000 cu m (5 lb BOD_5/day/1,000 cu ft) are impractical because of the oxygen requirement (30).

Parker indicates the most difficult problem in treating spent vegetable tannings appears to be color removal (29). Color is not reduced by biological treatment. However, reductions were observed by blending the influent or effluent with lime waste waters or coagulating with chemicals (29).

Eye investigated aerobic-anaerobic treatment of waste from a sole leather tannery (32). Laboratory and pilot studies were conducted prior to the initiation of full-scale systems. Lime bearing beamhouse fractions were found to be readily clarified by adding an anionic polymer followed by sedimentation. With polymer additions of 10 mg/l, overflow rates of 75.2 cu m/day/sq m (1,600 gpd/sq ft) produced 90

percent suspended solids removals. Later, a lagoon with a three-day detention time was found to produce equivalent removals and was incorporated into the full-scale system.

Subsequent treatment of the clarified beamhouse waste water in aerobic-anaerobic lagoons created severe odor problems. The problem was eliminated when spent vegetable tanning solution was combined with the beamhouse fractions for treatment. Removals observed through the biological system were as follows (32):

	Influent mg/l	Effluent mg/l	Removal %
BOD_5	1,146	152	87
Suspended Solids	408	105	74
COD	2,221	717	68
Sulfide	17	13	24
Total Kjeldahl Nitrogen (approximate)	150	100	33

High removals in BOD_5 (87 percent) and suspended solids (74 percent) indicate the wastes are amenable to aerobic-anaerobic treatment. The removals were obtained at volumetric loadings of 32.4 to 324 kg BOD_5/day/1,000 cu m (2 to 20 lb BOD_5/day/1,000 cu ft). Pilot operations indicate loading intensities ranging from 324 to 405 kg BOD_5/day/1,000 cu m (20 to 25 lb BOD_5/day/1,000 cu ft) are feasible (32). Total BOD_5 removal through the system averaged 90 percent. Lower removals were experienced in winter operations when the lagoon temperature was about 1°C (34°F). Sulfide removal was minimal in the system, which is contrary to other investigations (29). A kjeldahl nitrogen removal of 30 to 40 percent indicates nitrification in the aerobic portion of the lagoon.

Foaming periodically creates operation problems. High pressure water sprays are utilized to control foam during summer operations. Defoaming chemicals may be required during low temperature operation.

In Eye's tests (32), biological activity did not remove color. Color could be precipitated before or after biological treatment by elevating the pH to 11.5 or greater with lime and the addition of an anionic polymer.

Nitrification-denitrification is possible in multi-stage systems (32) (33). For this to occur, significant nitrification is required in a first stage aerobic operation. Feeding the nitrified waste to the anaerobic zone of the second stage lagoon denitrifies the waste. In the

absence of oxygen, anaerobic bacteria reduce the nitrate liberating nitrogen gas as a respiration product.

Aerobic-anaerobic lagoons offer several advantages, including (32): relatively small land requirements, low sludge volumes, reduced air requirements since organics are decomposed in the anaerobic zone, heat conservation during winter operation, and a potential for some nitrification-denitrification. Specific applications will require extensive pilot studies for evaluation of design parameters, particularly in regard to nitrification-denitrification.

On-Site Treatment - Activated Sludge Systems - The activated sludge process is perhaps the most innovative and flexible of all secondary treatment systems. It is applicable to almost all treatment situations. With proper operational control, high organic removals are possible. Designs based on solids retention time (SRT) afford optimum residence time for solids with minimal hydraulic detention period. However, extensive pilot studies are required to establish appropriate design parameters defining the relative rate of biological growth and decay. Basically, the activated sludge process consists of (34): mixing of returned activated sludge with the waste to be treated; aeration and agitation of the mixed liquor for the required length of time; separation of the activated sludge from the mixed liquor; and disposal of the excess sludge. Activated sludge is often preceded by some form of pretreatment. Variations in these processes create numerous operational phases. Overall efficiencies are highly dependent upon the monitoring and control provided by operating personnel.

Presented in Table 14 are results of full-scale and pilot activated sludge systems treating tannery wastes. Based on the effluent characteristics, operating difficulties are plaguing full-scale activated sludge facilities. At present, no facility is in operation that attains high removal efficiencies on a consistent basis. An exemplary facility does not exist.

TABLE 14

ACTIVATED SLUDGE SYSTEMS

System	Total Flow cu m/day (mgd)	BOD_5 Inf. mg/l	BOD_5 Eff. mg/l	BOD_5 Removal %	Suspended Solids Inf. mg/l	Suspended Solids Eff. mg/l	Suspended Solids Removal %	Total Nitrogen Inf. mg/l	Total Nitrogen Eff. mg/l	Total Nitrogen Removal %	Tannery	Process	Remarks	Reference
Screening, plain sedimentation, activated sludge, final sedimentation, sludge dewatering with pressure filters, land disposal	3,785 (1)	1,364	325	76	2,966	325	89		175		S. B. Foot Tanning Co., Red Wing, Minnesota	Cattle, pulp, chrome	Low removals since biological units not in full operation.	(10) (21)
Screening, plain sedimentation, activated sludge, final sedimentation	61 (0.016)	1,437	96	93	3,135	223	93	490	356	27	Caldwell Lace Leather, Auburn, Kentucky	Cattle, pulp, combination tanning	Primary and secondary clarifier overflow rates 11.8 and 10.5 cu m/day/sq m (290 and 258 gpd/sq ft), respectively. Aeration time 1.6 days.	(37)
Activated sludge, final clarification	1,514 (0.4)	1,700	343	80	2,400	190	92	286	180	37	Moench Tanning Co., Gowanda, New York	Cattle, save chrome	Volumetric loading on biological unit 3,712 kg/day/1,000 cu m (229 lb BOD_5/day/1,000 cu ft). Final clarifier overflow rate 20.4-24.4 cu m/day/sq m (500-600 gpd/sq ft).	(10)
Plain sedimentation, activated sludge, final clarification	Variable	2,500*		74-97	2,500*		30-91				Prime Tanning Co., Berwick, Maine	Cattle	Pilot study of flows from 0.09 to 0.19 l/sec (1.5 to 3 gpm). Volumetric loading from 1,751-4,409 kg/day/1,000 cu m (108-272 lb BOD_5/day/1,000 cu ft). Primary clarifier overflows 8.1-17.9 cu m/day/sq m (200-440 gpd/sq ft) and final clarifiers 12.2-22.0 cu m/day sq m (300-540 gpd/sq ft).	(43)

*Order-of-magnitude values.

Tannery #10 is in the process of initiating full facility operations for an estimated 3,785 cu m/ day (1 mgd) flow from a chrome tanning, hair pulp facility and finishing operations. The project is partially financed through an Environmental Protection Agency grant.

The combined tannery flows are screened, then pumped to dual plain sedimentation basins. The 10.7 m (35 ft) diameter clarifiers are equipped with surface skimmers. Overflow rates are approximately 21.6 cu m/day/sq m (460 gpd/sq ft) under present conditions. A potential of four concrete lined lagoons may be utilized for activated sludge aeration basins. Each lagoon has a capacity of about 3,785 cu m (1 mg) at 1.8 m (6 ft) operating depth. The depth may be varied in operation. Separate controls permit series, parallel, or a combination of lagoon operations. An aeration capacity of 22.3 kw (30 hp) per lagoon was initially indicated; however, a higher capacity may be required. Return sludge design permits recycle to each lagoon as well as ahead of the primary clarifiers. Aeration is followed by final sedimentation in two 12.2 m (40 ft) diameter clarifiers. The effluent is chlorinated prior to discharge to a nearby water course. Primary and waste activated sludge will be dewatered in a pressure filter and landfilled on-site. Automatic samplers permit monitoring of individual treatment units to ensure better operational control. The data presented in Table 14 represents only partial operation of this facility. Operating data to be developed should be beneficial to the industry due to the numerous operating ranges and controls provided in the system.

A full-scale activated sludge plant in Kentucky, Tannery #14, was evaluated in a two-week study by the Environmental Protection Agency (37). This tannery is a cattlehide tannery with pulp hair beamhouse operations and a combination of alum, chrome, and vegetable tanning. At the time of the study, flow was only 61 cu m/ day (0.016 mgd) of an anticipated 136 cu m/day (0.036 mgd) operation. The treatment system consists of screening, primary sedimentation, activated sludge, and secondary sedimentation. Overflow rates of 13.6 and 13.4 cu m/day/sq m (290 and 285 gpd/sq ft) were observed in primary and secondary units, respectively. Average hydraulic detention time was 1.6 days in the aeration basin. The following efficiencies were observed during operations:

	Influent mg/l	Effluent mg/l	Removal %
BOD_5	1,437	96	93
Suspended Solids	3,135	223	93
COD	4,016	481	88
Sulfide (as S)	7.9	0	100
Total Kjeldahl Nitrogen (as N)	490	322	34
Organic Nitrogen (as N)	328	175	47
Ammonia Nitrogen (as N)	162	147	9
Nitrite (as N)	0.1	34*	---
Nitrate (as N)	0.1	0.4	---
Alkalinity (as $CaCO_3$)	516	141	73

*Grab Sample

The BOD_5 cf the effluent was below 100 mg/l, indicating a removal of 93 percent at a volumetric loading of 908 kg/day/1,000 cu m (56 lb BOD_5/day/1,000 cu ft). Althcugh suspended solids reductions were high (93 percent), the effluent concentration was slightly above 200 mg/l. Apparent clarification difficulties exist. The COD was reduced 88 percent. Sulfides were completely oxidized in the aeration basin. The low removal of kjeldahl nitrogen (34 percent) shows minimal nitrificatiocn occurred even at the extended aeration time of 1.6 days. The possible toxic effects of high ammonia concentrations on nitrifying bacteria is indicated as a cause for the low removal (37). The alkalinity of the effluent was 114 mg/l with a pH of 7.3

An activated sludge facility in New York State (Tannery #15), is presently treating effluent frcm save hair beamhouse, chrome tan, and finishing operations. Total waste water from these processes is about 1,514 cu m/day (0.4 mgd). Combined flows are screened prior to equalization and adjustment of pH to 11.0. In some instances addition of lime is required. The equalization basin has a 24-hour capacity under present conditions. The unclarified discharge from the equalization basin is directed to an aeration basin with approximately 12 hours detention with a volumetric load on the basin of about 3,566 kg/day/1,000 cu m (220 lb BOD_5/day/1,000 cu ft). The final clarifier has an cverflow rate of 23.5 to 28.2 cu m/day/sq m (500 to 600 gpd/sq ft).

An organic removal of 80 percent produced an effluent BOD_5 concentration of 343 mg/l. Suspended solids reductions of 92 percent are reported. Effluent suspended solids concentrations of 190 mg/l reflect ineffective solids capture in the final clarifier. The pH of the effluent is 8.0-8.5. The most interesting aspects of these treatment operations are the high pH of waste entering the aeration basin and the high mixed liquor suspended solids concentration maintained in the aeration basin. Normally, a pH above 11.0 is indicated as potentially toxic to biological activity. However, carbon dioxide derived from organism respiration is adequate to reduce the pH to about 8.0, at which level biological conversions proceed. Since primary clarification is not provided, all suspended solids in the tannery waste go directly to the aeration basin. All solids capture must, therefore, occur in the final clarifier.

Another biological treatment innovation is the oxidation ditch. The oxidation ditch is essentially a modified form of the activated sludge system. Applications of this process on domestic waste treatment are numerous in Europe. Pilot studies indicate a potential for high strength tannery waste treatment.

As proposed for tannery treatment, clarified wastes are directed to an oval ditch or "race track" for aeration. Separate equalization facilities are not required, since the ditch provides excellent equalization (13). An adjustable speed brush rotating across the full width of the channel imparts oxygen to the waste water and regulates the velocity of flow in the channel. The effluent is clarified prior to discharge with the sludge returned to the aeration zone. The oxidation ditch provides a much larger aeration volume than conventional activated sludge. The resulting F/M ratio is very small. At these low F/M ratios (0.05) and long detention time, endogenous respiration minimizes the amount of waste sludge.

A pilot operation treated portions of the flow from a side leather tannery utilizing 25,060 kg/day of green salted hides (55,200 lb/day). The tanning process produced 1,800 cu m/day (0.475 mgd) of waste water from pulp hair, chrome tan, and finishing operations. The average flow to the pilot facility was 5 percent of the tannery discharge, or 90 cu m/day (0.024 mgd). The pilot plant feed remained proportional to the fluctuating supply to provide realistic variations of flow. After proportioning, the waste water was pre-settled for 30 to 45 minutes, then discharged to the oxidation ditch. The primary sludge was thickened for 12 hours prior to dewatering on drying beds. Hydraulic detention time in the oxidation ditch varied from two to three days, and the rate of activated sludge return was estimated at 75 percent. Production of secondary sludge was about 0.3 kg (lb) dry solids/kg (lb) BOD_5 applied, or 0.55 kg (lb) dry solids/kg (lb) BOD_5 without primary sedimentation. The organic load on the ditch varied from 23.5-48.2 kg BOD_5/day (51.8 to 106.2 lb BOD_5/day). The oxygen supplied was about 1.5 times the average BOD_5 load, however. This was not sufficient for peak

demands. Adjustment of brush rotation and submergence to increase oxygen transfer may be required for peak demands. The following pilot efficiencies resulted during summer operation (13):

	Presettled Influent* mg/l	Effluent* mg/l	Removal* %
BOD_5	500-1,500	15	98
COD	1,000-2,300	7300	85
Sulfide	10-80	0	100
Chrome (Cr^{+++})	---	1	---
Total Nitrogen (as N)	250	60-150	40-76
Ammonia Nitrogen (as N)	100	45-125	0-50

*Order-of-magnitude

High removals of BOD_5 (98 percent) and COD (88 percent) result at the low F/M ratio. Sulfides were completely oxidized with brush aeration. Precipitation of chrome was highly effective with concentrations below 1 mg/l observed in the effluent. Nitrification was sporadic, with some denitrification through the liberation of free ammonia or nitrogen gas. The exact mechanism of removal was not indicated. In general, the oxidation ditch is an attractive modification to the activated sludge process. Highly effective removals in BOD_5, suspended solids, sulfides, and chrome are demonstrated under desirable summer temperatures. With the extremely low F/M ratio and adjustment for winter operations, large system volumes are required. The limiting factor on application appears to be the availability of land.

Activated sludge systems, including various modifications, have been and can be effective in organic reductions with BOD_5 removals in excess of 90 percent and effluent concentrations below 100 mg/l. Removals of suspended solids appear to be critical with concentrations observed to be above 200 mg/l. Proper design and operation of final clarifiers may improve results; however, further treatment is indicated for significantly higher efficiencies. The nitrification potential of activated sludge systems has not been investigated at present facilities. Although feasible in theory, direct application to tannery wastes in pilot or full-scale facilities is non-existent.

Practical Biological Systems

Several tanneries do have biological treatment systems that are partially effective. However, the treatment systems have not maintained high levels of effluent reduction.

Plant 383 in subcategory 1 employs aerated lagoons to attain a BOD discharge of 1.9 kg/kkg (lb/1000 lb). Plant 24 in subcategory 3 utilizes a trickling filter plus aerated lagoons to achieve a BOD discharge of 1.0 kg/kkg (lb/1000 lb). The average effluent BOD concentration of sampled data and industry data is 32 mg/l. Plant 47 in subcategory 3 has an activated sludge system with lagoons. The BOD and SS discharger are 0.4 and 1.1 kg/kkg (lb/1000 lb) respectively. The BOD effluent concentration from both sampled data and industry data is 16 mg/l. Tannery 54 in subcategory 5 utilizes an anaerobic/aerobic lagoon system to achieve a BOD and SS discharge of 1.7 kg/kkg (lb/1000 lb). Industry data indicated a BOD concentration of 20 mg/l. Plant 179 employs lagoons to attain a BOD and SS discharge of 2.7 and 1.5 kg/kkg lb/1000 lb) respectively. Plant 43 in subcategory 2 utilizes lagoons to achieve a BOD discharge concentration of 38 mg/l (industry data) or 30 mg/l (sampled data). Three other tanneries (185,400 and 447) report a BOD concentration of 50 mg/l or less.

Although these systems are partially effective, there is no present on-site tannery treatment facility which can achieve a high level of effluent reduction of all major pollutants on a consistent basis. Thus, an exemplary tannery treatment system does not exist and the best practicable control technology currently available is not the average of the discharge from the best tannery waste treatment systems. The best practicable control technology currently available is an integration of present tannery waste treatment experience with performance data transferred from other industrial treatment operations, such as from the meat packing industry. The unit operation and unit processes combined to achieve the best practicable effluent reduction are as follows:

Waste Flow

Screening
Equalization
Primary Settling
Aeration
Secondary Settling

Sludge

Collection
Thickening
Disposal

This particular arrangement has been chosen not only because it is a practical approach to treatment, but because it is one system applicable to each of the six subcategories. The system could utilize activated sludge or trickling filters or anaerobic or aerobic lagoons cr an oxidation ditch depending on the individual tannery requirements.

Parameters used for design of principal items of equipment employing activated sludge are as follows:

Equalization Basin	Detention: 24 hours at design flow
Primary Settling	Overflow Rate: 20.4 cu m/day/sq m (500 gpd/sq ft)
Secondary Settling	Overflow Rate: 12.2 cu m/day/sq m (300 gpd/sq ft)
Aeratic Basin	F/M Ratio: 0.5 MLVSS: 4,000 mg/l BOD_5 Reaction Rate Constant: 0.0015
Deep Bed Filtration Unit	Flow Rate: 0.16 cu m/min/sq m (4 gpm/sq ft)
Waste Sludge	Primary: 2 percent solids Secondary: 1 percent solids Mixture thickened to 2.5 percent solids
Vacuum Filter	Loading Rate: 12.2 kg/sq m/hr (2.5 lb/sq ft/hr)

One factor concerning treatment requires special consideration and is included in design considerations: most treatment plants have had difficulty with residual suspended solids in the treated effluent. To ensure that the effluent will contain a minimum residual of suspended solids, two factors are included in the proposed design:

1. A low overflow rate of 12.2 cu m/day/sq m (300 gpd/sq ft) in the secondary settling tank.

2. Provision for the addition of polymers to the secondary settling tank as an aid to clarification.

Polishing Systems for Biological Treatment - Consideration has been given tc unit operations and process techniques which have been used infrequently or not at all in tannery waste treatment. They are as follows:

1. Filtration or microscreening of the effluent.

2. Carbon adsorption.

3. Color removal.

One problem experienced consistently with secondary treatment of tannery wastes is the high suspended solids content of the plant effluent. In some instances, this has been well over 100 mg/l. Undoubtedly, some of this may be due to poor design or poor operation. Nevertheless, there appears to be some evidence that filtration or microscreening may be effective in correcting this problem.

There are at the present time numerous applications of suspended solids removal by filtration or microscreening being used as a tertiary treatment process following conventional secondary biological treatment. However, there is no known application of this waste water treatment process existing in the tannery industry.

A microscreen consists of a rotating drum with a fine screen mounted on its periphery. Waste enters the drum through the open end and passes through the screen leaving the suspended solids on the inner surface of the screen. At the top of the drum, pressure jets of effluent water are directed into the screen to remove the mat of deposited solids. Numerous applications of microscreening of secondary waste water effluent illustrates from 55 to 99 percent removal of suspended solids.

With the exception of gravity sedimentation, deep-bed filtration is the most widely used unit process for liquid-solids separation. Deep-bed filters have been employed in systems for phosphorous removal from secondary effluents and in physical - chemical systems for the treatment of raw waste water.

Waste containing suspended solids is passed through the filter containing granular material resulting in the capture of suspended solids in the bed. Eventually, the pressure drop through the bed becomes excessive or the ability of the bed to remove suspended solids is impaired. The filtration cycle is terminated and the bed is backwashed prior to being placed back into service. In an ideal filter, the size of the particles should decrease uniformly in the direction of flow. This condition is partially achieved with the use of a multimedia deep bed filter. This type of filter utilizes materials with different densities ranging from the large size particles at the top of the filter having the lowest density and the smallest particles at the bottom of the filter having the highest density. With this arrangement, the filter has a large storage capacity for suspended solids, and is able to remain in operation for longer periods of time. Influent solids should be limited to about 100 mg/l to avoid too frequent backwashing. Effluent suspended solids are normally less than 10 mg/l.

Carbon adsorption using activated carbon in fixed beds is highly effective in the removal of organic dissolved solids, many of which are

non-biodegradable. The granular carbon media provides an effectively large surface area for adsorption. Biodegradation of the captured material further increases the efficiency of the process. Thermal regeneration is used to reactivate spent carbon.

Laboratory analysis were made on carbon treatment of waste water from Tannery #16 (52). These laboratory tests were preformed on waste that had been pretreated by pressurized aeration for sulfide removal and air flotation/clarification for oil and suspended solids removal. Results of these tests indicate that carbon adsorption can provide an effluent essentially free of suspended solids and colloidal material. The pilot plant effluent contained approximately 300 mg/l total organic carbon (TOC). The full-scale design is indicated as having a potential of reducing the effluent to less than 135 mg/l TOC representing approximately 80 percent reduction in oxygen demanding materials (52). A carbon exhaustion rate of 1.25 kg carbon per cu m (10.5 lb of carbon/1,000 gallons) of pretreated waste water is anticipated for this removal efficiency.

Activated carbon is effective in color removal. Vegetable tanning and dyeing operations contribute substantially to effluent color. Color exists as both a soluble constituent and colloidal suspension. The pilot study at Tannery #16 produced a 95 percent reduction in color (52). Tomlinson, et al., (53) observed a 90 percent reduction in color from laboratory studies of spent dye liquors at Tannery #14. Color was effectively removed at 2 to 4 grams of carbon/liter of spent dye liquors (53).

Activated carbon may have limited application in tannery treatment since removals are confined to dissolved organic solids such as spent dyes and tannin liquors. As an alternative to secondary treatment, carbon adsorption requires extensive pretreatment to effectively remove suspended solids that retard the adsorption of dissolved material. The process would not materially reduce the high content of dissolved inorganic materials such as sodium chloride (NaCl).

The problem of color of tannery waste is most pronounced in those systems using vegetable tanning. Color is an optical effect. The measured magnitude of color is not necessarily related to a weight quantity of the heterogeneous mixture of materials which is its cause. Because of the nature of the color, several investigators (20) (54) have suggested the use of APHA cobalt-platinum to be impractical. The hue and tint of vegetable tanning solutions are different from color standards. Therefore, several arbitrary approaches have been developed to determine percent of color removed in a particular unit operation. For this reason, further development of a standard is necessary. Nevertheless, it is necessary that color removal be incorporated in any treatment process for vegetable tanning wastes.

In no case observed or reported in the literature is a completely effective system for color removal in operation. This does not mean that such a system does not exist, but only that data is not readily available. Data on activated carbon presented previously indicates the anticipated performance of a full-size plant for carbon removal. Eye (32) and Hagan (20) have both determined that addition of 2,000 mg/l of lime and 2 mg/l of anionic polymer to plant waste would produce 90 percent color removal. The resulting pH of the waste was 11.5.

In many tanneries, the beamhouse waste can provide the major portion of the lime requirements.

Major Reduction of All Forms of Nitrogen

The need for limiting the amount of the nitrogen compounds entering rivers and lakes has been receiving increased attention. The concern is for the fixed nitrogen and not elemental nitrogen. Forms of fixed nitrogen include the following:

1. Organic nitrogen.

2. Ammonia and ammonium salts.

3. Nitrates.

4. Nitrites.

Normally, nitrites are not of major concern since they are readily oxidized to nitrate or reduced to nitrogen gas by the environment. All nitrogen forms can be considered as a nutrient source for plant life including the simpler forms such as algae. Ammonia can be toxic to fish and lower animals. Organic nitrogen can be converted to ammonia in the stream and produce the same results. Ammonia entering a stream will exert an oxygen demand. Organisms will convert ammonia to nitrate utilizing stream dissolved oxygen. One mg/l of ammonia nitrogen reacts with 4.5 mg/l of oxygen. Therefore, a serious oxygen depletion of the stream could occur with only a small ammonia concentration in the waste. All of these factors emphasize the need for consideration of nitrogen control.

Waste from the tannery contains nitrogen in both the organic and ammonia forms. Organic and ammonia are reported together as total kjeldahl nitrogen (TKN). Organic nitrogen in waste comes principally from the unhairing operation resulting from removal of protein degradation products. Where an amine is used in the unhairing operation it contributes to the total organic nitrogen. Some ammonia is formed in the unhairing operation by further breakdown of protein material. However, the major source of ammonia is ammonium sulfate in the waste stream from the bating process. TKN content of the total plant waste stream can be over 900 mg/l in some tanneries. The organic nitrogen

portion of the TKN can vary. One tannery (55) reports organic nitrogen content equal to about 60 percent of the TKN. During detention periods hydrolysis or other mechanisms convert organic nitrogen to ammonia. A large portion of the organic nitrogen is present in colloidal materials.

The following processes have been used for nitrogen removal:

1. Coagulation, flocculation, and settling.

2. Ammonia stripping.

3. Ammonia ion exchange.

4. Chlorination.

5. Biological nitrification-denitrification.

Coagulation, flocculation and settling is effective in partial removal of soluble and colloidal protein matter. To optimize this process, pH must be reduced to the isoelectric point of the protein, which is usually in the range of 4.5 to 5.0. At that point, the protein matter is least soluble. Some coagulant addition may be necessary to provide good settling.

Ammonia stripping has been applied to municipal waters where the ammonia nitrogen content is normally in the range of 15 to 30 mg/l. The pH of the waste must be increased to 11.0. No data is available for tannery waste. Even at the lower ammonia concentrations 3.0 cu m of air is required per liter of waste (400 cu ft/gal) (56).

Difficulties encountered in municipal waste treatment include serious calcium carbonate scaling and the reduced efficiency at low air temperatures. As the air temperature approaches 0° C (32° F) the system becomes essentially ineffective. Removal efficiency is 90 to 95 percent under optimum conditions but organic nitrogen is not affected by ammonia stripping.

Ammonia can also be removed from waste water by an ion exchange media which is a natural zeolite, clinoptilclite. This material is selective for the ammonium ion in the presence of ions such as calcium, magnesium, and sodium found in waste water. For the high ammonia content of tannery waste, capital investment for such a system would be high. Also, the presence of only a small concentration of large organic molecules can cause serious fouling and degradation with commonly used ion exchange media. Whether or not this fouling would pose a problem with the selective ion exchange media used for tannery waste has not been established.

Chlorination can be used to convert ammonia to nitrate. However, at a dosage of 10 mg/l of chlorine per mg/l of ammonia nitrogen, the cost is excessive except for very small concentrations.

In a biological system for removal of nitrogen, all organic nitrogen must be hydrolyzed to ammonia or be converted to a form from which it can be oxidized along with the ammonia present to nitrate. In the activated sludge process, a part of the ammonia and organic nitrogen is converted to nitrate. A higher conversion is accomplished in a system where the F/M ratio is low. Ammonia is converted to nitrite by a Nitrosomonas organism; nitrite is converted to nitrate by a Nitrobacter organism. These autotrophic microorganisms have a slow growth rate. One source (57) indicated that even an extended aeration activated sludge plant could not provide complete nitrification on a year-round basis. In activated sludge plants treating tannery wastes, TKN is reduced about 35 percent. Data for one plant is cited (55).

To be effective, the nitrification must be performed in a separate biological system with a nitrification basin followed by a settling tank. Optimum pH is 8.3 to 8.5. The organisms utilize an inorganic source of carbon (carbon dioxide or bicarbonate) and obtain energy from the ammonia oxidation reaction.

The nitrate nitrogen content of tannery wastes treated by the biological nitrification process is high. Nitrate nitrogen is essentially the same level as the ammonia nitrogen in the raw waste plus any organic nitrogen that is hydrolyzed prior to treatment. To remove this nitrate, a biological denitrification step in the treatment is required. This can be accomplished under anaerobic conditions by denitrifying organisms. Equipment required is a nitrification basin followed by a clarification tank. Optimum pH is 6.5 to 7.5. Organisms using a source of organic carbon convert the nitrate to nitrogen gas. Since the waste is normally lacking in organic carbon, methanol is added to provide such a source. Rate of addition is about 3 kg of methanol per kg (3 lb/lb) of nitrate nitrogen. Essentially complete denitrification is accomplished. If organic nitrogen is present, it will be unaffected.

Since there has been no experience with major removal of all forms of nitrogen in the tanning industry, these biological processes are used for the design and economic studies covered later herein. Details concerning design criteria for nitrification-denitrification processes are described in a design seminar paper (58).

Design criteria used are as follows:

Nitrification

Temperature 10°C (50°F)

MLVSS*: 5,000 mg/l

pH: 8.4

Loading Factor: 438 kg/day/1,000 cu m
(27 lb NH3-N/day/1,000 cu ft)

Loading: 65 percent of raw waste NH3-N

Denitrification

Temperature: 10°C (50°F)

MLVSS*: 3,000 mg/l

pH: 7.5

Loading Factor: 530 kg/day/1,000 cu m
(33.7 lb NC3-N/day/1,000 cu ft)

*Mixed Liquor Volitile Suspended Solids

Major Removal of All Waste Constituents

The major removal of all waste constituents refers to those processes which remove dissolved solids. Tannery waste waters, after extensive chemical and biological treatment, still contain a high concentration of inorganic salts. These salts are principally sodium chloride, calcium bicarbonate, calcium sulfate, and calcium hydroxide. Calcium hydroxide used in the unhairing operation reacts with ammonium sulfate and sulfuric acids from the bating and pickling operations to form calcium sulfate. Residual lime in waste is removed directly by settling or precipitated by respiration carbon dioxide. Some minor quantities of salts are present in the water supply. The major part of dissolved inorganic solids is introduced from the raw hides or processing solutions. Sodium chloride is present in the incoming hides as a preservative. It is also present in the pickling operation. Dissolved solids concentrations prior to treatment may range from 6,000 mg/l - 38,000 mg/l, with an expected average of 10,000 mg/l (10).

Unit treatment operations for removal of dissolved solids include the following:

1. Freezing.

2. Evaporation.

3. Electrodialysis.

4. Ion exchange.

5. Reverse osmosis.

Most of these processes produce a brine solution which requires further concentration and special disposal.

Freezing - Freezing is a non-selective method of dissolved solids removal. During freezing, ice crystals of pure water are formed. The dissolved constituents are forced to the periphery of the crystal platelets and adhere to the surface. The brine film is removed from the surface of the crystals by washing. The ice-brine separation has previously caused operational difficulties. A more effective wash is required, and also one that does not create a high volume of brine for ultimate disposal.

The freezing process has been proposed for treatment of clarified tannery discharge at a tannery (10). However, to date no full-scale operations have been implemented. Extensive pilot scale studies are required prior to expenditures for full-scale facilities. Freezing will have limited application in tannery treatment until all phases of the process are proven reliable.

Evaporation - This process is perhaps the oldest method for removal of dissolved solids. In principal, a saline solution is evaporated with heat energy. The vapor produced is mineral free and condensed for disposal or reuse. A strong brine solution alone or with some salt crystallization remains for disposal.

Solar energy may provide the required heat of evaporation when wastes are retained in large lagoons. However, climatic conditions coupled with relatively high continuous flows and the need for impervious soil or sealant imposes severe restrictions on the geographic location for such lagoons.

Multiple effect evaporators have been used in industry for many applications. A saline solution is heated to the boiling point, normally at an elevated pressure. The steam produced is directed to cooling in a second stage where the latent heat is used to evaporate more solution. This arrangement is used for a number of stages. Evaporation is carried out in each successive stage. A triple effect evaporator for salt concentration will evaporate slightly over two kg (lb) of water per kg (lb) of steam used.

Electrodialysis - Electrodialysis is a demonstrated process for removal of dissolved solids in brackish waters. Basically, the electrodialysis cell consists of alternate cationic and anionic permeable membrances in a stack alternately charged by electrodes at each end. An external power source maintains the potential across the electrodes. Based on the charge, an ion will migrate towards the oppositely charged electrode, but will be selectively captured between the membrane stacks. Relatively pure water remains between alternate membranes while the

concentrated waste brine collects in others. For waters of concentration less than 10,000 mg/l, the energy requirement in an actual installation is of the order of 2.6 to 7.9 kwhr per cu m (10 to 30 kwhr per 1,000 gallons) of product water (59). This is less than the energy required for the distillation process. The principal disadvantages for tannery applications are membrane fouling, polarization, and scaling from waste constituents. At present, there is no record of tanneries using the electrodialysis process.

Ion Exchange - This process is one in which there is an interchange of ions between the liquid being treated and a solid particulate media. The media is normally a zeolite or synthetic resin. Major application has been in water softening where a salt regenerated cation unit removes calcium and magnesium ions from the water and replaces them with sodium ions.

For salt removal from tannery wastes both a cation and an anion exchanger must be used. To make ion exchange economically feasible for desalination of water, special ion exchanger arrangements have been used. One of these is the DESAL process which is a three bed system (60). Two of these beds contain anion exchange media and the third contains a cation exchange media. The operation method is such that only stoichiometric quantities of regenerates are used, thereby providing substantial economy over operation of standard demineralization equipment.

A suitable method must be used to dispose of spent regenerant solutions. According to one manufacturer of ion exchange media, this process is generally applicable to solutions containing less than 3,000 mg/l of ionizable solids. Based on this fact and that resin fouling occurs from even small quantities of organic matter, application for treatment of tannery waste which has a salt content of well over 3,000 mg/l, waste is not considered feasible.

Reverse Osmosis - Reverse osmosis is a process which is non-selective with respect to dissolved solids removal and is reasonably dependable. In osmosis, when a salt solution and a pure solvent or a solution of less concentration are separated by a semi-permeable membrane, the pure solvent flows through and dilutes the salt solution. The process continues until equilibrium is established. The semipermeable membrane allows the pure solvent to pass, but not the solution. The driving force is the strong chemical potential of the pure solvent. The pressure developed in the process is the osmotic pressure. In reverse osmosis, a pressure applied to the salt solution in excess of the osmotic pressure forces the pure solvent through the membrane leaving a concentrated brine. The success of the system is dependent upon selection and maintenance of the membrane. Reverse osmosis has been effective for the treatment of pulp and the paper mill wastes, acid mine drainage, and municipal supplies with a high mineral content.

Pilot treatment of dilute pulp and paper effluents (61) produced membrane rejections of 90-99 percent for most feedwater components. Optimum performance is indicated at dissolved solids concentrations of 5,000 to 15,000 mg/l. The resulting brine solution was 8 to 10 percent solids.

Pilot scale studies on acid mine drainage (62) produced a product water with 10 mg/l dissolved solids from an influent containing 1,280 mg/l dissolved solids. Product water or permeate was about 75 percent of the total flow. The permeate did not meet drinking water standards.

An extensive pilot plant study was performed in California at the Pamona Water Rennovation Plant (63). This study demonstrated reverse osmosis obtained excellent rejection of dissolved solids from the effluent of a waste treatment plant using activated sludge and from a parallel plant using a granular activated carbon bed. Effluent from both systems contained a dissolved solids concentration of about 1,150 mg/l. The permeate contained 55 mg/l dissolved solids producing a 95 percent removal. Ammonia nitrogen and nitrate were reduced 95 percent and 75 percent respectively. The ammonia nitrogen in the effluent was about 15 to 20 mg/l.

There has been no direct application of reverse osmosis for treatment of tannery waste water. Investigations in the pulp and paper industry indicate that wastes of similar concentration are amenable to reverse osmosis. At these dissolved solids concentrations, the osmotic pressures encountered are high requiring higher applied pressures. There are several reasons reverse osmosis may be more appropriate than other methods discussed for the treatment of tannery wastes. The equipment is easy to operate. Energy requirements are relatively low. Also, an elevated operating temperature is not required. The process is non-selective in dissolved solids capture producing a high purity product water. The principal disadvantage is a large volume of low concentrated brine. Membrane fouling has been cited as a potential operational problem. Although not proven specifically for treating tannery wastes, it has been selected as the most applicable for this study based on data available. It will be necessary to prove by a demonstration project that this is a viable process for this application.

Design is based on a projected 75 percent recovery of usable water with a dissolved solids content of less than 500 mg/l. This is an interpolation based on present experience of a 25 percent recovery with sea water (3.5 percent salt) and an approximate 90 percent recovery with brackish water containing 3,000 mg/l of dissolved solids (64).

Disposal of waste brine from the reverse osmosis process can create a major problem. The waste brine constitutes 25 percent of the waste treated.. Further treatment prior to ultimate disposal is required. Research in advanced waste water treatment and desalination has produced

methods for handling brines. A few of the techniques investigated are as follows:

1. Various types of solvent extration.

2. Electrodialysis.

3. Solar evaporation.

4. Multiple effect evaporation.

5. Submerged combustion.

The various solvent extraction techniques for brine concentrations are not fully developed for practical application at this time.

Electrodialysis has shown the capability of brine concentrations to 200,000 mg/l (64). However, practical application requires further development.

Solar evaporation ponds are normally the most economical means for disposal of waste brines, however, their application is restricted to areas where evaporation exceeds annual rainfall by over 20 inches. These areas are principally in the west to southwest. Unfortunately, most tanneries are located in the northeast, southeast, and midwest, where humid climates make such operations unpractical.

Multi-stage flash evaporators are applicable for concentrating waste brines prior to ultimate disposal. The method is economical for concentrating solids up to 10 percent. Higher concentrations require multi-effect evaporators. Submerged combustion may be utilized to concentrate brines beyond saturation yielding crystal formation (65).

None of these processes have been demonstrated on brine from tannery waste. However, no special problems are anticipated. The principal problem is ultimate disposal of the concentrate if a salt is not crystallized and removed. Several possibilities exist for ultimate disposal of concentrated brine;

1. Deep-well disposal.

2. Ocean disposal.

3. Complete evaporation.

Deep-well disposal of brines requires comprehensive geologic study and field testing of potential disposal zones to assess the safety and effectiveness of underground strata. Several potential dangers exist for such disposal including pollution of fresh water supplies through encroachment and disturbance to underground strata. Injection wells

normally require detailed investigations to ensure that liquids in the underground strata are compatible both physically and chemically to the waste brines injected. Usually high pressure pumping is required for deep-well disposal.

Ultimate disposal in such reservoirs as the ocean may be feasible, Normally, tanneries are not located in close proximity to the ocean so that direct discharge is possible. Transport costs make ocean disposal from most tanneries economically unattractive.

For study purposes, a triple-effect evaporator is used for salt crystallization followed by filtration and drying. The recovered salt can be marketed for reuse.

Complete evaporation of the brine appears to be the most generally applicable approach to the problem.

The impact of disposal of waste brines from the tannery industry as well as those from other industries is likely to be a major problem in future years as higher degrees of treatment are implicated. Further study is required to determine methods of disposal of brines.

In the tanning industry, a substitute for salt in the hide curing process and increased reuse of process chemicals would be a major step in eliminating this problem.

SECTION VIII

COST, ENERGY, AND NON-WATER QUALITY ASPECTS

Cost and Reduction Benefits of Alternative Treatment and Control Technologies

A detailed economic analysis showing the impact of treatment and control technologies upon the six subcategories within the leather tanning and finishing industry is given in Supplement A of this document. Five alternative treatment methods have been considered for Subcategories 1 to 6. For the six subcategories, the alternatives include:

Alternative A - No waste treatment or control.

Alternative B - Preliminary treatment and chrome removal

Alternative C - Alternative B plus activated sludge.

Alternative D - Alternative C plus sulfide removal, nitrification, and denitrification and filtration.

Alternative E - Alternative D plus reverse osmosis, and evaporation.

Tables 15-20 illustrate the cost of waste water treatment for the average size plants in each subcategory. Both investment and total annual costs are shown for the various alternatives.

Basis of Economic Analysis - Following is a summary of the basis for cost estimates presented in Tables 15-20.

1. Investment - Investment costs have been derived principally from published data on waste water treatment plant construction costs (66) (67), Stanley Consultants' cost data, and information from equipment manufacturers and suppliers.

   Published cost data for treatment facilities is derived primarily from experience with waste water treatment installations. Cost information has been reported by some tanneries, but the data are not extensive enough to serve as a basis for the estimates presented herein. Basic data were developed by preparation of graphical relationships between cost and size for each unit operation. Based on treatment plant configuration, design criteria, and size, costs for individual unit operations were added together to determine major facility costs.

An allowance of 15 percent of the total investment has been included to cover land, contingencies, engineering, and overhead.

August, 1971 price levels have been chosen by the Environmental Protection Agency and are used herein as the base level for economic evaluation. Inflation since August, 1971, has had a marked impact on the cost of treatment facility construction, labor, and other costs involved in this analysis as well as raw and finished product prices. Inflationary trends should be taken into consideration when evaluating the costs presented herein in comparison with current costs.

2. Depreciation and Cost of Capital (Interest) - It was assumed that the annual interest costs (cost of capital) and depreciation would be constant over the life of the treatment facilities. A principal repayment period of 20 years was used. Costs were depreciated on a straight line basis and the depreciation period of 20 years was assumed equal to the principal repayment period and the economic life of the facilities.

   Cost of money was assumed to be an average of the cost of debt capital and the cost of equity capital. Cost of debt capital was assumed to be 8 percent and the cost of equity capital 22 percent. Data for the last 10 to 12 years indicates that the average net return on equity capital for the chemical industry and other manufacturing has been 10 to 12 percent. Assuming corporate income tax is equal to net return (50 percent of gross return), gross return is estimated to be 22 percent. Sixty percent of the investment was assumed to be debt capital and 40 percent equity capital. From this analysis, an average rate for the cost of money equal to 13.6 percent was determined. An average annual value for cost of money was derived by subtracting the straight line depreciation cost from the investment cost, times the capital recovery factor. The costs were about 8 percent of the capital investment.

3. Insurance and Taxes - An annual cost of 1 1/2 percent of the initial investment was used for insurance and taxes on the waste treatment plant.

4. Operation and Maintenance Labor - Operation and maintenance labor manhour requirements were based mainly on published data (66) (67) and independent estimates. The operational requirements include general management and supervisory personnel, equipment operators and laborers, and clerical and custodial personnel. Maintenance labor includes mechanical, electrical, laborers, and other appropriate repair personnel.

Based on labor rates in the tanning industry and municipal waste water treatment plants (68) (69), an August, 1971, average labor rate of $4.90 per hour (including fringe benefits) was used to compute total annual operation and maintenance labor costs. The costs were approximately 10 percent of the capital investment.

5. Chemicals - Chemical costs used in the economic analysis are based on published literature typical in the U. S. (70). The costs used are:

   Methanol - $0.069 per liter ($0.26 per gallon)

   Lime - $22.00 per metric ton ($20.00 per ton)

   Soda Ash - $3.96 per 100 kilograms ($1.80 per 100 pounds)

   Ferric Chloride - $8.80 per 100 kilograms ($4.00 per 100 pounds)

   Polymer - $0.44 per kilogram ($0.20 per pound)

   Chlorine - $13.20 per 100 kilograms ($6.00 per 100 pounds)

   Sulfuric Acid - $36.40 per metric ton ($33.00 per ton)

   Ferric Sulfate - $46.30 per metric ton ($42.00 per ton)

   Sodium Hydroxide (50%) - $8.50 per 100 kilograms ($3.85 per 100 pounds)

   Manganous Sulfate - $90.50 per metric ton ($82.00 per ton)

6. Energy - In broad context, energy includes electric power and fuel. Electric power consumption for major units such as aeration. pumping, and mixing was estimated from available data (66) (67). An allowance of ten percent was made for small power users such as clarifiers, chemical feed equipment, ventilation equipment, and so forth. The cost of electric power was assumed to be $0.015/kwhr.

   For Alternative E, steam is required for evaporation, dewatering, and drying of the waste brine. The cost of steam ranged from $1.76 to $2.42/1,000 kg of steam ($0.80 to $1.10/1,000 lb of steam).

TABLE 15

WASTE WATER TREATMENT COSTS (1)
FOR SUBCATEGORY 1

PARAMETER/COST	ALTERNATIVE (4) B	C	D	E
PLANT RAW MATERIAL PRODUCTION				
1000 kg hides/mo	636	636	636	636
(1000 lb hides/mo)	1,400	1,400	1,400	1,400
EQUIVALENT FINISHED PRODUCT(2)				
1000 sq m hides/mo	88	88	88	88
(1000 sq ft hides/mo)	950	950	950	950
AVERAGE FLOW				
l/kg hide	33	33	33	33
(gal/lb hide)	4	4	4	4
ESTIMATED INVESTMENT COST(3)				
($1000)	$361.5	$683.8	$1,073.1	$2,473.1
ESTIMATED ANNUAL INVESTMENT				
$/1000 kg hides/yr	47.3	89.5	140.6	323.8
($/1000 lb hides/yr)	21.5	40.7	63.9	147.2
ESTIMATED ANNUAL COST				
($1000)	$88.6	$167.6	$262.9	$718.9
$/sq m hide	0.084	0.159	0.249	0.681
($/sq ft hide)	0.008	0.015	0.023	0.063
TYPICAL FINISHED PRODUCT				
Price ($/sq ft hide)	0.640	0.640	0.640	0.640
TREATMENT COST AS PERCENT OF PRODUCT PRICE	1.25	2.3	3.6	9.8

(1) All Costs Based on August 1971 Price Levels

(2) Raw Material Conversion Factor to Finished Product = 0.68 $\frac{\text{sq ft}}{\text{lb}}$

(3) Assumes Treatment Facilities Sized to Meet Plant Production with No Allowance for Growth

(4) ALTERNATIVE B = Preliminary Treatment (Chrome Removal)
ALTERNATIVE C = Alternative B plus Activated Sludge
ALTERNATIVE D = Alternative C plus Sulfide Removal, Nitrification and Denitrification, and Filtration
ALTERNATIVE E = Alternative D plus Reverse Osmosis and Evaporation

TABLE 16

WASTE WATER TREATMENT COST (1)
FOR SUBCATEGORY 2

PARAMETER/COST	ALTERNATIVE (4) B	C	D	E
PLANT RAW MATERIAL PRODUCTION				
1000 kg hides/mo	863	863	863	863
(1000 lb hides/mo)	1,900	1,900	1,900	1,900
EQUIVALENT FINISHED PRODUCT(2)				
1000 sq m hides/mo	120	120	120	120
(1000 sq ft hides/mo)	1,290	1,290	1,290	1,290
AVERAGE FLOW				
l/kg hide	50	50	50	50
(gal/lb hide)	6	6	6	6
ESTIMATED INVESTMENT COST(3)				
($1000)	$517.2	$886.7	$1,342.2	$3,697.2
ESTIMATED ANNUAL INVESTMENT				
$/1000 kg hides/yr	49.7	85.6	129.6	356.8
($/1000 lb hides/yr)	22.6	38.9	58.9	162.2
ESTIMATED ANNUAL COST				
($1000)	$126.8	$217.2	$328.8	$1,073.8
$/sq m hide	0.088	0.151	0.228	0.746
($/sq ft hide)	0.008	0.014	0.021	0.069
TYPICAL FINISHED PRODUCT				
Price ($/sq ft hide)	0.640	0.640	0.640	0.640
TREATMENT COST AS PERCENT OF PRODUCT PRICE	1.25	2.2	3.3	10.8

(1) All Costs Based on August 1971 Price Levels

(2) Raw Material Conversion Factor to Finished Product = 0.68 $\frac{\text{sq ft}}{\text{lb}}$

(3) Assumes Treatment Facilities Sized to Meet Plant Production with No Allowance for Growth

(4) ALTERNATIVE B = Preliminary Treatment (Chrome Removal)
ALTERNATIVE C = Alternative B plus Activated Sludge
ALTERNATIVE D = Alternative C plus Sulfide Removal, Nitrification and Denitrification, and Filtration
ALTERNATIVE E = Alternative D plus Reverse Osmosis and Evaporation

TABLE 17

WASTE WATER TREATMENT COSTS (1)
FOR SUBCATEGORY 3

PARAMETER/COST	ALTERNATIVE (4) B	C	D	E
PLANT RAW MATERIAL PRODUCTION				
1000 kg hides/mo	431	431	431	431
(1000 lb hides/mo)	950	950	950	950
EQUIVALENT FINISHED PRODUCT(2)				
1000 sq m hides/mo	51	51	51	51
(1000 sq ft hides/mo)	550	550	550	550
AVERAGE FLOW				
l/kg hide	42	42	42	42
(gal/lb hide)	5	5	5	5
ESTIMATED INVESTMENT COST(3)				
($1000)	$284.0	$528.3	$821.1	$2,828.1
ESTIMATED ANNUAL INVESTMENT				
$/1000 kg hides /yr	54.8	101.9	158.4	545.6
($/1000 lb hides /yr)	24.9	46.3	72.0	248.0
ESTIMATED ANNUAL COST				
($1000)	$ 69.6	$129.4	$201.2	$ 590.2
$/sq m hide	0.114	0.211	0.329	0.964
($/sq ft hide)	0.010	0.020	0.030	0.089
TYPICAL FINISHED PRODUCT				
Price ($/sq ft hide)	0.780	0.780	0.780	0.780
TREATMENT COST AS PERCENT OF PRODUCT PRICE	1.3	2.6	3.8	11.4

(1) All Costs Based on August 1971 Price Levels

(2) Raw Material Conversion Factor to Finished Product = 0.58 $\frac{\text{sq ft}}{\text{lb}}$

(3) Assumes Treatment Facilities Sized to Meet Plant Production with No Allowance for Growth

(4) ALTERNATIVE B = Preliminary Treatment (Chrome Removal)
ALTERNATIVE C = Alternative B plus Activated Sludge
ALTERNATIVE D = Alternative C plus Sulfide Removal, Nitrification and Denitrification and Filtration
ALTERNATIVE E Alternative D plus Reverse Osmosis and Evaporation

TABLE 18

WASTE WATER TREATMENT COSTS (1)
FOR SUBCATEGORY 4

PARAMETER/COST	ALTERNATIVE (4) B	C	D	E
PLANT RAW MATERIAL PRODUCTION				
1000 kg hides/mo	341	341	341	341
(1000 lb hides/mo)	750	750	750	750
EQUIVALENT FINISHED PRODUCT(2)				
1000 sq m hides/mo	84	84	84	84
(1000 sq ft hides/mo)	900	900	900	900
AVERAGE FLOW				
l/kg hide	17	17	17	17
(gal/lb hide)	2	2	2	2
ESTIMATED INVESTMENT COST(3)				
($1000)	$177.3	$314.3	$466.6	$986.6
ESTIMATED ANNUAL INVESTMENT				
$/1000 kg hides/yr	43.3	76.8	114.0	241.2
($/1000 lb hides/yr)	19.7	34.9	51.8	109.6
ESTIMATED ANNUAL COST				
($1000)	$43.5	$76.9	$114.3	$267.3
$/sq m hide	0.043	0.076	0.113	0.265
($/sq ft hide)	0.004	0.007	0.010	0.025
TYPICAL FINISHED PRODUCT				
Price ($/sq ft hide)	0.610	0.610	0.610	0.610
TREATMENT COST AS PERCENT OF PRODUCT PRICE	0.7	1.1	1.6	4.1

(1) All Costs Based on August 1971 Price Levels

(2) Raw Material Conversion Factor to Finished Product = 1.2 $\frac{\text{sq ft}}{\text{lb}}$

(3) Assumes Treatment Facilities Sized to Meet Plant Production with No Allowance for Growth

(4) ALTERNATIVE B = Preliminary Treatment (Chrome Removal)
ALTERNATIVE C = Alternative B plus Activated Sludge
ALTERNATIVE D = Alternative C plus Sulfide Removal, Nitrification and Denitrification and Filtration
ALTERNATIVE E = Alternative D plus Reverse Osmosis and Evaporation

TABLE 19

WASTE WATER TREATMENT COSTS (1)
FOR SUBCATEGORY 5

PARAMETER/COST	ALTERNATIVE (4) B	C	D	E
PLANT RAW MATERIAL PRODUCTION				
1000 kg hides/mo	148	148	148	148
(1000 lb hides/mo)	325	325	325	325
EQUIVALENT FINISHED PRODUCT (2)				
1000 sq m hides/mo	66	66	66	66
(1000 sq ft hides/mo)	715	715	715	715
AVERAGE FLOW				
l/kg hide	62.5	62.5	62.5	62.5
(gal/lb hide)	7.5	7.5	7.5	7.5
ESTIMATED INVESTMENT COST (3)				
($1000)	$249.5	$388.7	$560.4	$1,299.4
ESTIMATED ANNUAL INVESTMENT				
$/1000 kg hides/yr	140.8	219.3	316.1	733.0
($/1000 lb hides/yr)	64.0	99.7	143.7	333.2
ESTIMATED ANNUAL COST				
($1000)	$61.2	$95.2	$137.2	$363.2
$/sq m hide	0.077	0.120	0.173	0.459
($/sq ft hide)	0.007	0.011	0.016	0.042
TYPICAL FINISHED PRODUCT				
Price ($/sq ft hide)	0.48	0.48	0.48	0.48
TREATMENT COST AS PERCENT OF PRODUCT PRICE	1.5	2.3	3.3	8.8

(1) All Costs Based on August 1971 Price Levels

(2) Raw Material Conversion Factor to Finished Product = 2.2 $\frac{\text{sq ft}}{\text{lb}}$

(3) Assumes Treatment Facilities Sized to Meet Plant Production with No Allowance for Growth

(4) ALTERNATIVE B = Preliminary Treatment (Chrome Removal)
ALTERNATIVE C = Alternative B plus Activated Sludge
ALTERNATIVE D = Alternative C plus Sulfide Removal, Nitrification and Denitrification and Filtration
ALTERNATIVE E = Alternative D plus Reverse Osmosis and Evaporation

TABLE 20

WASTE WATER TREATMENT COSTS (1)
FOR SUBCATEGORY 6

PARAMETER/COST	ALTERNATIVE (4) B	C	D	E
PLANT RAW MATERIAL PRODUCTION				
1000 kg hides/mo	499	499	499	499
(1000 lb hides/mo)	1,100	1,100	1,100	1,100
EQUIVALENT FINISHED PRODUCT (2)				
1000 sq m hides/mo	70	70	70	70
(1000 sq ft hides/mo)	750	750	750	750
AVERAGE FLOW				
l/kg hide	17	17	17	17
(gal/lb hide)	2	2	2	2
ESTIMATED INVESTMENT COST(3)				
($1000)	$254.4	$408.4	$692.4	$1,374.4
ESTIMATED ANNUAL INVESTMENT				
$/1000 kg hides/yr	42.5	68.0	115.5	229.0
($/1000 lb hides/yr)	19.3	30.9	52.5	104.1
ESTIMATED ANNUAL COST				
($1000)	$62.3	$100.0	$169.6	$408.6
$/sq hide	0.074	0.119	0.202	0.486
($/ sq ft hide)	0.007	0.011	0.019	0.045
TYPICAL FINISHED PRODUCT				
Price ($/sq ft hide)	0.31	0.31	0.31	0.31
TREATMENT COST AS PERCENT OF PRODUCT PRICE	2.3	3.5	6.1	14.5

(1) All Costs Based on August 1971 Price Levels

(2) Raw Material Conversion Factor to Finished Product = 0.68 $\frac{\text{sq ft}}{\text{lb}}$

(3) Assumes Treatment Facilities Sized to Meet Plant Production with No Allowance For Growth

(4) ALTERNATIVE B = Preliminary Treatment (Chrome Removal)
ALTERNATIVE C = Alternative B plus Activated Sludge
ALTERNATIVE D = Alternative C plus Sulfide Removal, Nitrification and Denitrification and Filtration
ALTERNATIVE E = Alternative D plus Reverse Osmosis and Evaporation

Effluent Reduction - Subcategory 1 - The following discussion for Subcategory 1 deals with the sensitivity of effluent reduction with respect to costs for Subcategory 1. This subcategory represents a substantially larger segment of the industry than any other subcategory. Costs are based on an average size tannery in this subcategory processing 29,510 kg (65,000 lb) of hides per day.

Alternative A - No Waste Treatment or Control

The estimated organic waste load for Subcategory 1 is 95 kg BOD_5/1,000 kg (95 lb BOD_5/1,000 lb) of hide. This represents 14 times that of normal domestic sewage.

Costs - None.

Reduction Benefits - None.

Alternative B - Preliminary Treatment and Chrome Removal

This alternative includes in-process chromium removal, pumping, screening, equalization, and primary clarification. Sludge handling includes holding tanks and thickening units, Effluent waste loads from this alternative are estimated to be 47 kg BOD_5/1,000 kg (47 lb BOD_5/1,000 lb) of hide processed. Reduction of oil and grease, and chromium also occur.

Costs - The total capital investment cost is estimated to be $361,500 for the model plant. The annual treatment cost is estimated to be less than $90,000.

Reduction Benefits - Alternative B represents about a 50 percent reduction in BOD_5 compared with Alternative A. Total reduction in BOD_5 with preliminary treatment would, therefore, be 50 percent. Other constituents are also removed as noted.

Alternative C Alternative B Plus Activated Sludge

This alternative provides the same units as pretreatment with the addition of an aeration basin and secondary clarifier. The effluent waste load is estimated at 2.7 kg BOD_5/1,000 kg (2.7 lb BOD_5/1,000 lb) of hide processed for the average Subcategory 1 tannery treatment facility.

Costs - Alternative C represents a total capital investment of $683,800 and an annual cost of $167,600. These costs represent an increase of $322,000 in capital costs and almost $80,000 in annual costs over Alternative B.

Reduction Benefits - Alternative C represents a reduction in BOD_5 of 94 percent over Alternative B. This represents a total reduction in plant BOD_5 of 97 percent.

Alternative D - Alternative C Plus Sulfide Removal, Nitrification and Denitrification, and Filtration

Alternative D includes the treatment units for Alternative C with the addition of a sulfide removal process, nitrification basin, covered denitrification basin, sulfide removal process, aeration flume, and a graded media filter. The effluent from the average Subcategory 1 tannery treatment facility would be 1.35 kg BOD_5/1,000 kg (1.35 lb BOD_5/1,000 lb) of hide processed. Significant removal of sulfide and nitrogen would also result.

Costs - Alternative D represents a total capital investment of $1,073,100 and an annual cost of $262,900. These costs represent an increase of almost $390,000 in capital costs and about $95,000 in annual costs over Alternative C.

Reduction Benefits - Through Alternative D, there is an incremental reduction in BOD_5 of 50 percent over Alternative C. Total reduction in BOD_5 would be about 98.5 percent. Sulfide and nitrogen removals also result.

Alternative E - Alternative D Plus Reverse Osmosis, and Evaporation

Alternative E includes the same operations as Alternative D with the addition of a reverse osmosis unit for the removal of dissolved solids, evaporation facilities for concentration of the rejection water from the reverse osmosis unit, and dewatering-drying facilities for the waste brine. In addition to these, the final clarifier in Alternative D would be replaced by a reactor clarifier with provisions for soda ash addition to soften prior to reverse osmosis and evaporation. Reverse osmosis product water and condensed evaporator water would be recycled to the tannery wet processes. Alternative E would result in zero discharge and no liquid wastes to the receiving streams.

Costs - The capital investment is estimated to be $1,400,000 more than Alternative D and annual costs are estimated to be over $450,000 more than Alternative D.

Reduction Benefits - There would be an incremental reduction in BOD_5 of 100 percent over that of Alternative D, or a total reduction in plant BOD_5 load of 100 percent. All other constituents would be completely removed.

Impact of Waste Treatment Alternatives on Finished Product Price

Tables 15-20 illustrate the probable increases in finished product prices for the six subcategories to pay for waste water treatment. For the best practicable control technology currently available, estimated increases in final product costs range from 1.1 to 3.5 percent for various subcategories. For only one subcategory is the increase in excess of 2.6 percent.

For the best available control technology economically achievable, the estimated increase of final product cost ranges from 0.5 to 2.6 percent for various subcategories and only one subcategory is in excess of 1.3 percent.

The overall cost of both best practicable and best available control technology is estimated to increase final product costs from 1.6 to 6.1 percent for various subcategories and only one subcategory is in excess of 3.8 percent.

Alternative Treatment Systems

It has been assumed in the economic analysis that an activated sludge process will be utilized for the biological treatment. However, aerobic or aerobic-anaerobic lagoons can be designed to provide the same degree of biological treatment. These lagoons require substantial areas and can only be utilized where land is readily available near the tannery. Lagoons may result in cost savings of almost $150,000 over those costs presented for Alternative C.

The estimated waste treatment costs for each subcategory are given in Tables 15-20. The total investment cost estimated for the leather tanning and finishing industry is $28 million for best practicable control technology currently available limitations (see Table 21), and $42.5 million or an increment of $14.5 million for best available control technology economically achievable limitations (see Table 22).

The 1977 investment consists of $28.0 million for processors outside municipal systems. including about $7 million each for subcategories 1 and 3, about 6 million each for subcategories 2 and 5 and $1.4 million for subcategory 4. Distribution of 1983 costs is similar.

It is estimated that the current in-place treatment system investment is $11 million. No credit has been calculated for this in-place treatment in Tables 15-20 or Tables 21-22.

TABLE 21

ESTIMATED INDUSTRY INVESTMENT (1)
TO MEET BPCTCA EFFLUENT LIMITATIONS

SUBCATEGORY	PRODUCTION 10^6kg/yr(10^6lb/yr)	BPCTCA INVESTMENT $/1000 kg/yr($/1000 lb/yr)	PERCENT(2) AFFECTED	INVESTMENT ($1000)(3)
1	305(672)	18.5(40.7)	26	$7,100
2	149(328)	17.7(38.9)	46	$5,900
3	114(252)	21.0(46.3)	62	$7,200
4	66(145)	15.8(34.9)	27	$1,400
5	69(152)	45.3(99.7)	42	$6,400
6	18.9(41.7)	14.0(30.9)	0	-
		TOTAL INDUSTRY COST		$28,000

(1) All costs based on August 1971 price levels

(2) Percent of subcategory production discharging directly to receiving waters

(3) Assumes no in-place treatment capital

TABLE 22

ESTIMATED INDUSTRY INVESTMENT (1)
TO MEET BACTEA EFFLUENT LIMITATIONS

SUBCATEGORY	PRODUCTION 10^6 kg/yr (10^6 lb/yr)	BACTEA INVESTMENT $/1000 kg/yr ($1000 lb/yr)	PERCENT(2) AFFECTED	INVESTMENT ($1000)(3)
1	305(672)	(29.0(63.9)	26	$11,200
2	149(328)	26.7(58.9)	46	$ 8,900
3	114(252)	32.7(72.0)	62	$11,200
4	66(145)	23.5(51.8)	27	$ 2,000
5	69(152)	65.2(143.7)	42	$ 9,200
6	18.9(41.7)	23.8(52.5)	0	–
		TOTAL INDUSTRY COST (INCREMENTAL COST)		$42,500 ($14,500)

(1) All costs based on August 1971 price levels

(2) Percent of subcategory production discharging directly to receiving waters

(3) Assumes no in-place treatment capital

Related Energy Requirements of Alternative Treatment and Control Technology

The energy requirements (electric power and fuel) for tanneries vary considerably based upon reported data. This variation is due to the following factors:

1. Type of hide tanned.

2. Type and extent of beamhouse, tan yard, and finishing operations.

3. Degree of mechanization within the tannery.

4. Climate of the tannery location.

Energy requirements for a typical Subcategory 1 tannery processing hide from raw material to finished product are approximately 0.46 kwhr/kg of hide (0.21 kwhr/lb) of electrical energy and 3,560 kg cal/kg of hide (6,700 Btu/lb) for steam. Following is a discussion of the additional power requirements for waste treatment Alternatives A through E.

There is no treatment provided by Alternative A, hence energy use is zero.

Alternative B treatment energy requirements are approximately 0.049 kwhr/kg (0.022 kwhr/lb) of hide. This represents about 10 percent of the tannery electrical energy demand, and about 1% of total energy required. The major units requiring this energy are the pumps and equalization tank mixers.

The treatment units in Alternative C require nearly 0.174 kwhr/kg (0.079 kwhr/lb) of hide processed. This represents a power use approximately 36 percent above that needed for Alternative B, and about 7.2% of total energy required. The major power demanding units in Alternative C are pumps, equalization tank mixers and aeration equipment.

The energy required for Alternative D treatment is 0.346 kwhr/kg (0.157 kwhr/lb) of hide. This is twice the energy required in Alternative C, and about 7.2% of total energy required. Major energy use is similar to that in Alternative C with the addition of recycle pumping and the aeration equipment for the nitrification basin and aeration flume.

The electric energy requirments for Alternative E total 0.374 kwhr/ kg (0.170 kwhr/lb) of hide. This amounts to an increase of approximately 8 percent over Alternative D and is due principally to requirements of the feed pumps for the reverse osmosis unit.

In addition to electrical requirements, steam is needed for evaporation and drying the salt. Steam requirements are about 3,820 kg cal/kg

(7,200 Btu/lb) of hide in the form of steam. This represents an increase of approximately 107 percent over the energy requirements of an average tannery (Subcategory 1) without treatment facilities.

Nonwater Quality Aspect of Alternative Treatment and Control Technology

Air Pollution - Particulate matter and hydrogen sulfide are the two potential causes of air pollution from the leather tanning and finishing process. Hydrogen sulfide is toxic even in low concentrations and is the main cause of process odor. Hydrogen sulfide is formed principally by reactions involving sulfide wastes from the unhairing process. Proposed in-process control includes oxidation of sulfides with a catalyst prior to discharge to the main plant sewers and treatment. This avoids any air pollution problems that could result from sulfides and improves the safety of workers in and around the treatment system. Use of biological systems to remove nitrogen instead of ammonia stripping also avoids potential air problems which could result from venting ammonia from the highly concentrated waste.

The major potential source of air particulate matter from a tannery is from hide buffing operations. However, most tanneries control this by wet scrubbing. Scrubber water is generally combined with the total waste stream. Several tanneries are adding buffing dust to sludge derived from liquid waste treatment for disposal.

In addition to process sources, tannery boilers can be a source of air pollution. With proper design and maintenance of gas and oilfired boilers, there should be no emission problems. However, with coal-fired boilers, fly ash emissions are a problem. Fly ash emissions can be kept to a minimum with proper design and operation. Dust collection equipment may be used to further control air pollution. Wet scrubbers or electrostatic precipitators are capable of providing in excess of 98 percent removal of the fly ash. If a wet scrubber is used, the waste dust slurry can be discharged to the waste water treatment system. Fly ash from the electrostatic precipitators can be combined with the dewatered sludge for disposal.

Boiler flue gas contains sulfur dioxide when the fuel burned in the boilers contains sulfur. Some coal and heavy fuel oils contain sulfur and emit sulfur dioxide when burned. Burning low sulfur fuel is one method of minimizing sulfur dioxide air pollution problems. Gas scrubbing devices for removal of sulfur dioxide are now in the development stages.

Solid Waste Disposal - Solid waste from tanneries and tannery wastewater treatment plants includes the following:

1. Fleshings.

2. Hair.

3. Raw hide trimmings.

4. Tanned hide trimmings.

5. Sanding and buffing dust.

6. Lime sludge.

7. Chrome sludge.

8. Biological sludge.

9. Grease

10. General plant waste.

Most tanneries recover fleshings and raw hide trimmings for sale to rendering plants or conversion into glue at the tannery site. Tanned hide trimmings are often sold as by-products. Office and general plant waste is either hauled away by a local refuse disposal service or disposed of on-site.

In save-hair operations, the tannery has facilities for washing, drying, and baling of the hair. The baled hair is sold as a by-product.

Sanitary landfills are best suited for disposal of tannery waste. Incineration and high temperature treatment are not recommended for sludges containing chrome, since chrome may be reduced from the trivalent to the hexavalent state.

Tannery sludges containing chrome should not be spread on the land until further efforts are made to define the impact of these waste materials upon the environment.

Alternatives B through E assume sludge disposal costs. Disposal includes hauling the dewatered sludge to a landfill as well as landfill operating costs. Anticipated for disposal in landfills are chemical, lime, chrome, and biological sludges.

The selection of a proper site for landfill operations is of prime consideration. Requirements in the selection include: sufficient area; reasonable haul distance; remote location relative to residential, commercial, and recreational developments; soil conditions and rock formations; accessibility to existing transportation networks; and proximity to existing grcundwater supplies. The soil cover should be sloped such that precipitation will run off rather than percolate and pollute groundwater sources. Other factors to be considered include provisions tc prevent the obstruction of natural drainage channels,

location to avoid flood waters, and the consideration of possible fire hazards.

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

GUIDELINES AND LIMITATIONS

General

The effluent limitations which must be achieved by July 1, 1977, are to specify the degree of effluent reduction attainable through the application of the Best Practicable Control Technology Currently Available. The best practicable control technology currently available is generally based upon the average of the best existing performance by plants of various sizes, ages and unit processes within the industry. This average is not based upon a broad range of plants within the leather tanning and finishing industry, but upon performance levels achieved by exemplary plants. In industrial categories where present control and treatment practices are uniformly inadequate, a higher level of control than any currently in place may be required if the technology to achieve such higher level can be practicably applied by July 1, 1977.

In establishing the best practicable control technology currently available effluent limitations guidelines, consideration must also be given to:

1. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application.

2. The age and size of equipment and facilities involved.

3. The processes employed.

4. The engineering aspects of application of various types of control techniques.

5. Process changes.

6. Non-water quality environmental impact (including energy requirements).

Also, best practicable control technology currently available emphasizes treatment facilities at the end of manufacturing processes, but includes control technologies within the process itself when the latter are considered to be normal practice within an industry.

A further consideration is the degree of economic and engineering reliability which must be established for the technology to be "currently available." As a result of demonstration projects, pilot plants, and general use, there must exist a high degree of confidence in

the engineering and economic practicability of the technology at the time of commencement of construction of installation of the control facilities.

Effluent Reduction Attainable

Based upon information contained in Sections III through VIII of this report, a determination has been made of the degree of effluent reduction attainable through the application of the best practicable control technology currently available. The effluent concentrations which could be achieved were estimated and applied to the respective water uses for each subcategory (see Table 7). BOD_5 and SS calculations are based on an effluent concentration of 50 mg/l; total chromium and oil and grease are based on 1 mg/l and 10 mg/l respectively. These values then determine the weight of pollutants per weight of product. Effluent limitation guidelines resulting from implementation of this technology are presented in Table 23. These are the recommended guidelines for each industrial subcategory for plants discharging directly to surface waters. The limitations require major removal of BOD_5 and suspended solids.

TABLE 23

BEST PRACTICABLE EFFLUENT LIMITATIONS
(July 1, 1977)

PARAMETER(1)	SUBCATEGORY kg/1000 kg hide (lb/1000 lb hide)					
	1	2	3	4	5	6
BOD_5	2.7	3.2	2.5	1.0	3.2	1.4
TOTAL CHROMIUM	0.05	0.06	0.05	0.02	0.06	0.03
OIL & GREASE	0.53	0.63	0.50	0.24	0.63	0.34
SS	3.0	3.5	2.8	1.1	3.5	1.5

(1) For all subcategories pH should range between 6.0 and 9.0 at any time

For all subcategories Most Probable Number (MPN) of Fecal Coliforms should not exceed 400 counts per 100 ml

Best Practicable Control Technology Currently Available

The best practicable control technology currently available for the leather tanning and finishing industry has previously been identified in Section VII (for Subcategories 1 through 6) under the headings "In-Process Methods of Reducing Waste," "Preliminary Treatment," and "Major Reduction of BOD_5 and Suspended Solids." Principal control and treatment operations needed to meet these limitations are generally summarized in Section VII. The effluent reduction attainable is based upon the transfer of performance data from other industrial treatment operations. Other industries such as the meat packing industry currently treat high strength wastes and achieve the high removal efficiencies required by BPCTCA. The required effluent quality is being achieved by the tanning industry but not on a consistent basis. Because the effluent quality representing that attainable through the implementation of BPCTCA is not achieved consistently, technology and performance information has been transferred from other industry treatment operations.

Complete Treatment - Subcategories 1 to 6

1. Recycle of chrome and vegetable tan solutions (where applicable).

2. Fine screening.

3. Equalization to dampen quality and quantity fluctuations which will impair subsequent processes, particularly biological units.

4. Primary settling to provide oil and grease separation, precipitate chromium from rinse waters, and partially remove BOD_5, COD, and suspended solids.

5. Aeration and secondary settling to further reduce BOD_5, COD, and suspended solids.

6. Sludge handling and disposal.

The above summary of treatment steps generally applies to Subcategories 1 through 6. A few minor alterations are required. One change in the steps includes addition of lime after primary settling for tanneries which have acid waste (sheepskin).

Rationale for Selection of the Best Practicable Control Technology Currently Available

Total Cost of Achieving Effluent Reduction Based upon information contained in Section VIII of this report, the leather tanning and finishing industry discharging to receiving waters would have to invest

an estimated $28 million (August, 1971, price levels) to achieve the effluent limitations recommended herein. No in-place treatment capital is assumed. The total annual costs for pollution control including depreciation, interest, and operation and maintenance will likely result in an increase in finished product price ranging from 1.1 to 3.5 percent for the various subcategories. For only one subcategory is the increase in excess of 2.6 percent.

Age and Size of Equipment and Facilities - As indicated previously in this report, there appears to be no significant data to substantiate that either the age or size of the tannery justify special consideration of different effluent limitations. Data indicates some of the oldest and smallest tanneries are currently achieving levels of treatment equivalent to those achieved by large new facilities.

Engineering Aspects of Control Technique Application

The specific level of technology is practicable because it is being practiced by plants in the tannery industry as well as other industries with high strength wastes. The tannery industry does not achieve this level of effluent reduction. One plant in subcategory 1 (383) and one plant in subcategory 3 (24) meet the BOD limitations in kg/1000 kg (16/1000 lb) but not TSS limits. Two plants in subcategory 3 (47 and 179) meet the TSS limitations and almost achieve the BOD limitation.

In terms of achieving a BOD effluent discharge of 50 mg/l, the following plants achieve this level of reduction: plant 43 in subcategory 2; plants 24 and 47 in subcategory 3; and plant 54 in subcategory 5. Tanneries 185, 400 and 447 also achieve an effluent discharge with less than 50 mg/l BOD. Thus, there are tannery plants that are capable of achieving the stated effluent limitations on a consistent basis. In a few cases, the presence of a knowledgable operator is the only requirement. In general, some minor plant design changes along with cooperation from management and plant personnel will be required.

Processes Employed - As indicated in earlier sections, there are differences in tanning processes which result in varying raw waste characteristics. These variations have been recognized by establishing six major industry subcategories for effluent limitations.

Process Changes - The control and technology required for implementing the best practicable control technology currently available does require some in-process changes for some tanneries. These modifications are principally chrome and vegetable tan solution reuse which are currently practiced by several industries.

Nonwater Quality Environmental Impact - There is one essential impact of waste treatment upon nonwater elements of the environment and this is disposal on the land of general tannery solid wastes and waste sludge

from treatment facilities. Most of the waste trimmings and hair from hides are being recovered as by-products. Reuse of chrome in the tannery will substantially reduce chrome levels in waste sludge from the treatment facility. This will also reduce the potential release of toxic chrome to the environment when the dewatered sludge cake is disposed of in a landfill. In all cases, however, dewatered sludges from chrome tanneries should be handled separately at a landfill to avoid any potential difficulties. Proper siting and operation of a landfill will minimize the impact of disposal of waste solids from the tannery on the land.

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE - GUIDELINES AND LIMITATIONS

General

The effluent limitations which must be achieved by July 1, 1983, are to specify the degree of effluent reduction attainable through the application of the "best available control technology economically achievable". The best available technology economically achievable is to be based on the very best control and treatment employed within the industry or based upon technology which is readily transferable to the industry. Since there are no exemplary facilities which may be considered for assessment of the best available control technology achievable control and treatment technology, transfer of concepts applied elsewhere are utilized.

Consideration must be given to the following in determining the best available control technology economically achievable:

1. The total cost of achieving the effluent reduction resulting from application of the best available control technology economically achievable.

2. The age and size of equipment and facilities involved.

3. The processes employed.

4. The engineering aspects of the application of various types of control techniques.

5. Process changes.

6. Non-water quality environmental impact (including energy requirements).

In contrast to the best practicable control technology currently available technology, the best available control technology economically achievable assesses the availability of in-process controls as well as additional treatment techniques employed at the end of a production process.

The best available control technology economically achievable is the highest degree of control technology that has been achieved or has been demonstrated to be capable of being designed for plant scale operation up to and including "no discharge" of pollutants. This level of control

is intended to be the top-of-the-line of current technology subject to limitations imposed by economic and engineering feasibility. The best available control technology economically achievable may be characterized by some technical risks with respect to performance and certainty of costs. Some further industrially sponsored development work prior to its application may be necessitated.

Effluent Reduction Attainable

Based upon the information contained in Sections III through VIII, an assessment has been made of the degree of effluent reduction which may be achieved through the application of best available technology. BOD_5 and SS calculations are based on an effluent concentration of 25 mg/l; total chromium and oil and grease are based on 1 mg/l and 10 mg/l respectively; and sulfide and total kjeldahl nitrogen are based on 0.1 mg/l and 5 mg/l respectively. Table 24 summarizes for each industrial subcategory the best available control technology economically achievable effluent limitations guidelines for facilities discharging directly to receiving waters. This limitation level is principally an extension of the best practicable control technology currently available requirements to provide for additional removals of BOD and SS as well as sulfide and nitrogen removal.

TABLE 24

BEST AVAILABLE EFFLUENT LIMITATIONS
(July 1, 1983)

PARAMETER(1)	SUBCATEGORY kg/1000 kg hide (lb/1000 lb hide)					
	1	2	3	4	5	6
BOD_5	1.35	1.60	1.25	0.50	1.60	0.70
TOTAL CHROMIUM	0.05	0.06	0.05	0.02	0.06	0.03
OIL & GREASE	0.53	0.63	0.50	0.24	0.63	0.34
SULFIDE	0.005	0.006	0.005	0.002	0.006	0.003
SS	1.5	1.8	1.4	0.6	1.8	0.8
TKN	0.27	0.32	0.25	0.10	0.31	0.14

(1) For all subcategories pH should range between 6.0 and 9.0 at any time

For all subcategories Most Probable Number (MPN) of Fecal Coliforms should not exceed 400 counts per 100 ml

Best Available Technology Economically Achievable

The best available technology economically achievable for the leather tanning and finishing industry (Subcategories 1 through 6) is removal of BOD and SS and sulfide and nitrogen reductions (as discussed in Section VII) in addition to those constituent removals established for the best practicable control technology currently available. Following is a general summary of the major steps required for achieving this level for a tannery providing complete treatment before discharge directly to surface waters. As with the best practicable control technology currently available, guidelines for the best available control technology economically achievable are based on control and treatment efficiencies achieved by some tanneries some of the time and by other industrial treatment operations on a consistent basis. With proper operation and adequate design, tanneries in each of the six subcategories can achieve the required effluent reduction.

Complete Treatment - Subcategories 1 to 6

1. Recycle of chrome and vegetable tanning solutions (where applicable).

2. Collection of beamhouse wastes containing sulfide; oxidation of sulfide using a catalyst such as manganous sulfate (where applicable).

3. Fine screening.

4. Equalization to dampen variations in quality and quantity which will impair subsequent processes, particularly biological units.

5. Aeration and clarification of solids to remove carbonaceous BOD_5, COD, and suspended solids.

6. Aeration to nitrify organic and ammonia nitrogen; mixing with a carbon source to cause denitrification; an aeration flume to assist nitrogen gas removal; and a final settling tank.

7. Filtration of the final effluent using deep-bed, mixed-media filters or similar devices for final suspended solids removal.

8. Sludge handling and disposal.

Rationale for Selection of the Best Available Technology Economically Achievable

Total Cost of Achieving Effluent Reduction - As presented in Section VIII, to meet the best available control technology economically achievable effluent limitations, tanneries discharging to receiving waters would have to invest an estimated $42.5 million (August, 1971, price levels). This $42.5 million includes the $28 million investment required to meet the best practicable control technology currently available guidelines and assumes no in-place treatment systems. The incremental cost is $14.5 million for treatment plants for processors outside municipal systems. Total annual costs (including depreciation, interest, operation and maintenance) to achieve these limitations are estimated to increase the cost of the finished product between 0.5 and 2.6 percent for various industrial classifications. Only one subcategory is in excess of 1.3 percent.

Age and Size of Equipment and Facilities - As indicated in Section IX, no differentiation of the effluent limitations guidelines can be made on the basis of age or size.

Processes Employed - Differences in processes within the industry have been accounted for in establishing the effluent limitations.

Engineering Aspects of Control Techniques - The best available control technology economically achievable appears achievable considering the developmental work being done on sulfide oxidation and nitrification-denitrification. There are several technical questions which need to be resolved prior to initiation of full-scale nitrification-denitrification facilities on a tannery waste. However, it is deemed that such questions can be answered by on-going research in other areas and by investigations initiated prior to 1983. To date, no pilot work has been reported for nitrification-denitrification of tannery waste, hence studies will be required to confirm design parameters required to implement an efficiently designed and operated facility.

Process Changes - Process changes required for the best available control technology economically achievable include those for the best practicable control technology currently available (see Section IX). In addition sulfide oxidation is recommended; its technical feasibility has been demonstrated on a pilot plant scale. The industry should initiate research to find potential substitutes for ammonium salts used in the bate operation and salt used for hide curing. These process changes would reduce treatment costs for the best available control technology economically achievable and also effect considerable reduction in dissolved solids which are economically very unattractive for removal in a waste treatment facility.

Nonwater Quality Environmental Impact - The impact upon the land as a result of liquid waste treatment is the same as outlined for the best practicable control technology currently available in Section IX.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

General

The standards of performance for new sources are to reflect the greatest degree of effluent reduction achievable through the application of the "best available demonstrated control technology, processes, operating methods, or other alternatives". New source is defined as any construction which is recommended after publication of the regulations prescribing the standards of performance. In addition to considering the best in-plant and end- of - process control technology identified for the best available control technology economically achievable, new source performance standards is to establish effluent reductions which may be achieved by changing or improving the production process itself. A determination must be made of whether a standard permitting no discharge of pollutants is practicable.

For establishing new source performance standards effluent limitations guidelines, consideration must also be given to:

1. The type of process employed and process changes.
2. Operating methods.
3. Batch as opposed to continuous operations.
4. Use of alternative raw materials and mixes of raw materials.
5. Use cf dry rather than wet processes (including substitution of recoverable solvents for water).
6. Recovery of pollutants as by-products.

Improved In-plant Process Control

For new sources of tanning wastes, several items may be considered to either reduce water use or discharge of waste to a treatment facility. Most of the possible changes are merely improvements on those which are already assumed capable of implementation for meeting the best practicable control technology currently available and the best available control technology economically achievable effluent limitations guidelines.

A new facility, due to more efficient layout and more automation, can effect better process control, thus minimizing water use and optimizing chemical use. In addition, general housekeeping procedures should

improve. The net effect of improved process layout, control and monitoring in a new tannery will mainly be to decrease water use and discharge of some chemicals. Organic loads resulting from hide processing are not expected to change, however. Hence, the waste discharge in kg (lb)/1,000 kg (lb) hide may not change significantly. Improved equipment and controls in a new plant merely reduce some of the tank sizes at the treatment facility utilized to meet the variable waste characteristics from a tannery not equipped with new equipment. For example, better scheduling and control of different types of waste may reduce the size of equalization facilities required to level out the quality and quantity of waste reaching a biological aeration tank. In addition, reduction of waste process chemicals may lower addition of neutralizing chemicals at the waste treatment facility.

Two chemicals employed in the production process that could substantially reduce the treatment needs if a substitute were found are ammonium salts used in bating and sodium salt from the hides. There is no indication that a significant change could be made for these, but it is recommended the industry research possibilities.

Use of dry processes or other drastic process modifications do not appear feasible for the tanning industry.

New Source Performance Standards

Although better process control and more efficient tannery operations may result for new facilities, the actual raw waste load in terms of kilograms (pounds) per thousand kilograms (pounds) of hide is not expected to change substantially. Treatability of the waste is also not likely to differ significantly from that existing for present facilities. Hence, standards of performance for new facilities should be set consistent with those required for the best practicable control technology currently available.

Pretreatment Requirements

Three constituents of the waste water from plants within the leather tanning and finishing industry have been found which would interfere with, pass through, or otherwise be incompatible with a well designed and operated publicly owned activated sludge or trickling filter waste water treatment plant. Waste water constituents include chromium from the tanning or retanning operation, sulfide from the unhairing process, and oil and grease from the fatliquour process or from animal fat. Adequate control methods can and should be used to keep significant quantities of these materials out of the waste water.

SECTION XII

ACKNOWLEDGMENTS

The Environmental Protection Agency wishes to acknowledge the contributions of the Stanley Consultants who prepared the original draft of this document. The efforts of Mr. Kenneth M. Bright, Mr. John L. Thomas and Mr. Robert L. Thoem are appreciated.

Special thanks and appreciation are due Mr. Irving R. Glass, President of the Tanners' Council of America; Professor William T. Roddy, Director of the Tanners' Council Research Laboratory, University of Cincinnati; and Mr. Robert M. Lollar, Coordinator for Environmental Affairs, Tanners' Council of America.

Appreciation is expressed for the interest of several individuals within the Environmental Protection Agency: W. L. Banks, Region VII; William Hancuff, George Webster, Ernst Hall, Allen Cywin, EGD.

Special thanks are due Richard Sternberg for his advice, support and guidance. Thanks are also due the many secretaries who typed and retyped this document: Aqua McNeal, Pearl Smith, Chris Miller, Vanessa Datcher, Karen Thompson, and Fran Hansborough.

Special acknowledgment is made of the contributions of industry personnel who provided information to the study. Their active response, cooperation and assistance is greatly appreciated.

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SECTION XIV

GLOSSARY

Acidity

A measure of the ability of the waste to provide hydrogen ions when treated with alkaline materials. Generally expressed in mg/l as $CaCO_3$.

ACT

The Act is the Federal Water Pollution Control Act Amendments of 1972.

Activated Sludge

A waste water treatment process using a mixed microbiological culture and molecular oxygen to satisfy waste stabilization requirements. Provision is made to return some solids settled from the effluent flow to the influent, and thereby maintain the desired microorganism population in the process.

Adipose

Of, or related to, animal fat; fatty.

Adsorption

The adhesion of a gas, liquid, or dissolved substance to the surface of a solid or liquid.

Aeration

A process for mixing and contacting air with water or liquid waste by natural or mechanical means.

Aerobic

A biological process in which oxygen is used for microorganism respiration needs. Especially relating to the degradation process of waste matter in the presence of dissolved oxygen.

Alkalinity

A measure of the ability of the waste to provide hydroxyl ion to react with acidic materials. Generally expressed in mg/l as $CaCO_3$.

Anaerobic

A biological process in which chemically combined oxygen is used for microorganism respiration needs. Relating to biological degradation of waste matter in the absence of dissolved oxygen.

Back

That portion of the animal hide, especially cattlehide, consisting of the center portion of the hide along the backbone and covering the ribs, shoulders, and butt (excluding the belly).

Bating

The manufacturing step following liming and preceding pickling. The purpose of this operation is to delime the hides, reduce swelling, peptize fibers, and remove protein degradation products from the hide.

Beamhouse

That portion of the tannery where the hides are washed, limed, fleshed, and unhaired when necessary prior to the tanning process.

Belly

That portion of the hide on the underside of the animal usually representing the thinnest part of the tannable hide.

Bend

That portion of the hide representing the entire hide cut down the backbone with the bellies and shoulders removed.

Best Available Demonstrated Control Technology

Treatment and control required for new sources of industrial discharge to surface waters as defined by Section 306 of the Act.

Best Available Technology Economically Achievable

Treatment and control required by July 1, 1983, for industrial discharges to surface waters as defined by Section 301(b)(2)(A) of the Act.

Best Practicable Control Technology Currently Available

Treatment and control required by July 1, 1977, for industrial discharges to surface waters as defined by Section 301(b)(1)(A) of the Act.

Biochemical Oxygen Demand (BOD5)

The amount of oxygen required by microorganisms while stabilizing decomposable organic matter under aerobic conditions. The level of BOD is usually measured as the demand for oxygen over a standard five-day period. Generally expressed as mg/l.

Blowdown

The amount of concentrated liquor wasted in a recycle system in order to maintain an acceptable equilibrium of contaminants in any process liquor.

Bluesides

A hide after tanning with chromium salts. Hide usually has a slight blue color.

Chemical Oxygen Demand (COD)

A measure of the amount of organic matter which can be oxidized to carbon dioxide and water by a strong oxidizing agent under acidic conditions. Generally expressed as mg/l.

Chlorine Contact Tank

A detention basin designed to allow sufficient time for the diffusion and reaction of chlorine in a liquid for disinfection purposes.

Chromium (Total)

Total chromium is the sum of chromium occurring in the trivalent and hexavalent state. Expressed as mg/l as Cr.

Clarification

A physical means for the removal of suspended particles in a liquid by gravity sedimentation (settling).

Coagulant

A substance which forms a precipitate or floc when added to water. Suspended solids adhere to the large surface area of the floc, thus increasing their weight and expediting sedimentation.

Collagen

The fibrous protein material within the hide which provides the bulk of the volume of the finished leather and its rigidity.

Colloids

Microscopic suspended particles which do not settle in a standing liquid and can only be removed by coagulation or biological action.

Color

A measure of the light absorbing capacity of a waste water after turbidity has been removed. One unit of color is that produced by one mg/l of platinum as K_2PtCl_6.

Coloring

A process step in the tannery whereby the color of the tanned hide is changed to that of the desired marketable product by dyeing or painting.

Composite Sample

A series of small waste water samples taken over a given time period and combined as one sample in order to provide a representative analysis of the average waste water constituent levels during the sampling period.

Concrete Mixer

A term often applied to hide processors.

Corium

The layer of hide between the epidermis and the flesh. Also called the derma.

Deliming

The manufacturing step in the tanhouse that is intended to remove lime from hides coming from the beamhouse.

Demineralization

The process of removing dissolved minerals from water by ion exchange, reverse osmosis, electrodialysis, or other process.

Derma

That part of the hide which is between the flesh and the epidermis.

Desalinization

The process of removing dissolved salts from water.

Detention (Retention)

The dwell time of waste water in a treatment unit.

Dewatering

The process of removing of a large part of the water content of sludges.

DO

Dissolved oxygen. Measured in mg/l.

Drum

A large cylinder, usually made of wood, in which hides are placed for wet processing. The drum is rotated around its axis, which is oriented horizontally. Also called wheel.

Electrodialysis

A form of advanced waste treatment in which the dissolved ionic material is removed by means of a series of semi-permeable membranes and electric current.

Enzyme

Complex protein materials added to the hide in the bating step in order to remove protein degradation products that would otherwise mar hide quality.

Epidermis

The top layer of skin; animal hair is an epidermal regrowth.

Equalization

The holding or storing of wastes having differing qualities and rates of discharge for finite periods to facilitate blending and achievement of relatively uniform characteristics.

Eutrophication

The excess fertilization of receiving waters with nutrients, principally phosphates and nitrates, found in waste water which results in excessive growth of aquatic plants.

Fatliquoring

The process of adding oils, fats, and greases (fatliquor) to tanned hides to improve and prevent cracking.

Finishing

The final processing steps performed on a tanned hide. These operations follow the retan-color-fatliquor processes, and include the many dry processes involved in converting the hide into the final tannery product.

Float

The proper level or volume of skins or hides, chemicals, and water that is maintained in any wet process unit (vats, drums, or processors) within the tannery.

Floc

Gelatinous masses formed in liquids by the addition of coagulants, by microbiological processes, or by particle agglomeration.

Flocculation

The process of floc formation normally achieved by direct or induced slow mixing.

Flume

An open, inclined channel or conduit for conveying water or water and hides.

Grab Sample

A single sample of waste water which will indicate only the constituent levels at the instant of collection; contrasted to a composite sample.

Graded Media Filter

A filtration device designed to remove suspended solids from wastewater by trapping the solids in a porous medium. The graded media filter is characterized by fill material ranging from large particles with low specific gravities to small particles with a higher specific gravity. Gradation from large to small media size in the direction of normal flow.

Grain

The epidermal side of the tanned hide. The grain side is the smooth side of the hide where the hair was located prior to removal.

Grease

A group of substances including fats, waxes, free fatty acids, calcium and magnesium soaps, mineral oils, and certain other non-fatty materials. The grease analysis will measure both free and emulsified oils and greases. Generally expressed as mg/l.

Green Hides

Hides which may be cured but have not been tanned.

Ion Exchange

The reciprocal transfer of ions between a solid and a solution surrounding the solid. A process used to demineralize waters.

Ionization

The process by which, at the molecular level, atoms or groups of atoms acquire a charge by the loss or gain of one or more electrons.

Liming

The operations in the beamhouse where a lime solution comes in contact with the hide. Liming in conjunction with use of sharpeners such as sodium sulfhydrate is used to either chemically burn hair from the hide or to loosen it for easier mechanical removal. Hair burning normally utilizes higher chemical concentrations.

Membrane

A semi-permeable barrier used in reverse osmosis and electrodialysis which allows water molecules and certain dissolved molecules to pass through it while impeding the passage of other dissolved solids.

Nitrogen, Ammonia

A measure of the amount of nitrogen which is combined as ammonia in waste water. Expressed in mg/l as N.

Nitrogen, Kjeldahl (Total Kjeldahl Nitrogen or TKN)

A measure of nitrogen combined in organic and ammonia form in wastewater. Expressed in mg/l as N.

Nitrogen, Nitrate

A measure of nitrogen combined as nitrate in waste water. Expressed as mg/l as N.

Nutrient

Any material used by a living organism which serves to sustain its existence, promote growth, replace losses, and provide energy. Compounds of nitrogen, phosphorus, and other trace materials are particularly essential to sustain a healthy growth of microorganisms in biological treatment.

Outfall

The final outlet conduit or channel where waste water or other drainage is discharged into an ocean, lake, or river.

Pack

Layers of salted hides formed at the slaughter house or hide curing firm (usually approximately 20 to 40 feet in area and 5 to 6 feet high).

Paddle Vat (Paddle)

A vat with a semi-submerged rotating paddle arrangement used for the mixing of water and chemicals with the hide.

pH

The reciprocal logarithum of the hydrogen ion concentration in wastewater expressed as a standard unit.

ppm

Parts per million. The expression of concentration of constituents in waste water; determined by the ratio of the weight of constituent per million parts (by weight) of total solution. For dilute solutions, ppm is essentially equal to mg/l as a unit of concentration.

Pasting

The process step generally following the retan-color-fatliquor operations whereby the hide is attached to smooth plates with a starch and water paste and dried in a controlled heated vessel.

Pickle

The process that follows bating whereby the hide is immersed in a brine and acid solution to bring the skin or hides to an acid condition; prevents precipitation of chromium salts on the hide.

Plating

The finishing operation where the skin or hide is "pressed" in order to make it smoother.

Polymer

An organic compound characterized by a large molecular weight. Certain polymers act as coagulants or coagulant aids. Added to the wastewater, they enhance settlement of small suspended particles. The large molecules attract the suspended matter to form a large floc.

Processor

A mixing apparatus resembling a concrete mixer which is used in some tanneries.

Pullery

A plant where sheepskin is processed by removing the wool and then pickling before shipment to a tannery.

Retan

The process step following tanning and any intermediate drying whereby hides which have not been fully tanned in the chrome tanning process may be retanned either with chrome, vegetable, or synthetic tanning agents. This operation generally precedes coloring and fatliquoring.

Reverse Osmosis

A process whereby water is forced to pass through semi-permeable membranes under high pressures. Water passing through the membrane is relatively free of dissolved solids; solids are retained in concentrated form on the feed side of the membrane and are wasted.

Sanding

A dry operation performed on the tanned and fatliquored hide in order to achieve the desired surface texture of the leather. Sanding operations include the use of abrasive or buffing wheels.

Scouring

A process where shearlings are washed.

Scudding

An operation following the major unhairing step where the last of the hair is removed from the hide.

Sedimentation

Clarification (settling).

Sharpeners

Chemicals used in addition to lime to assist in the unhairing process (such as sodium sulfide and sodium sulfhydrate).

Shearling

A lamb or sheepskin tanned with the hair retained.

Shoulder

That part of the hide which represents the shoulder of the animal.

Side

A side represents half a hide which has been cut along the spine.

Skiving

The thin layer shaved or cut off the surface of finished leather, principally sheepskin.

Sludge

A concentrate in the form of a semi-liquid mass resulting from settling of suspended solids in the treatment of sewage and industrial wastes.

Split

A side which has been cut parallel to its surface to provide one large piece of leather of approximately uniform thickness and a thin, smaller piece of nonuniform thickness called a split.

Staking

The finishing process wherein the hide or skin is stretched to make it more pliable and to avoid shrinkage. Tacking.

Standard Industrial Classification (SIC)

The numerical designation given to various industries by the Bureau of the Budget. The leather tanning and finishing industry bears SIC No. 3111.

Submerged Combustion

A flash evaporation type procedure used in the separation of dissolved solids from water.

Sulfide

Ionized sulfur. Expressed as mg/l as S.

Suspended Solids (SS)

Constituents suspended in waste water which can usually be removed by sedimentation (clarification) or filtration.

Tacking

Staking using tacks to fasten skins or hides to a large frame.

Tannin

The chemicals derived from the leaching of bark, nuts, or other vegetable materials used in the vegetable tanning process.

Tan Yard (Tan House)

That portion of the tannery in which the bating, pickling, and tanning is performed on the hides or skins.

Total Dissolved Solids (TDS)

The total amount of dissolved materials (organic and inorganic) in waste water. Expressed as mg/l.

Total Solids (TS)

The total amount of both suspended and dissolved materials in waste water. Expressed as mg/l.

Unhairing

The process where the hair is removed from the hide.

Volatile Solids

Solids, dissolved or suspended, which are primarily organic and during stabilization exert the significant portion of the BOD_5.

Weir

A control device placed in a channel or tank which facilitates measurement or control of the water flow.

Wheel

Drum.

METRIC UNITS

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by	TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram - calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	F°	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	t	0.907	kkg	metric tons (1000 kilograms)
yard	y	0.9144	m	meters

* Actual conversion, not a multiplier

Environmental Protection Agency
Library, Region V
1 North Wacker Drive
Chicago, Illinois 60606