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DRAFT

Supplement For Pretreatment to the Development Document for the

LEATHER TANNING AND FINISHING

Point Source Category

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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REVIEW NOTICE

This document presents conclusions of a study conducted for the Effluent Guidelines Division, United States Environmental Protection Agency, in support of draft pretreatment standards for the leather tanning and finishing industry.

The conclusions of this document may be subject to subsequent revisions during the document review process, and therefore may be superseded prior to final promulgation of the regulations in the Federal Register, as required by the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500).

DRAFT SUPPLEMENT

for

PRETREATMENT

to the

DEVELOPMENT DOCUMENT

for the

LEATHER TANNING AND FINISHING
POINT SOURCE CATEGORY

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ABSTRACT

This document presents the findings of an extensive study of the leather tanning and finishing industry by the Environmental Protection Agency for the purpose of developing pretreatment standards for the industry to implement Section 307(b) of the Federal Water Pollution Control Act Amendments of 1972 (the "Act").

The leather tanning and finishing plants included in this study are plants that manufacture leather and leather products from purchased hides or skins of cattle, sheep, pig, deer, horse, and other animals. There are seven subcategories in the leather tanning and finishing industry. These are based on similarities of processes and raw waste characteristics, particularly BOD_5 in kilograms per thousand kilograms, and flow in volume of wastewater generated per unit weight of hide, as raw material received.

Conclusions are set forth regarding wastewater quality improvement to protect personnel and facilities in municipal sewerage and treatment systems. These conclusions involve existing tanneries discharging into a municipal sewerage system. The total capital cost for existing tannery facilities, which discharge to municipal systems, is based only on sulfide removal and is estimated at $7.3 million.

Supportive data and rationale for development of the conclusions contained in this report are based on current information from 128 leather tanning and finishing plants and from the original development document and data record prepared for and by the EPA and published in March 1974.

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SECTION I

CONCLUSIONS

A conclusion of this study is that the leather tanning and finishing industry comprises seven subcategories:

1. Cattle-pulp-chrome tan.
2. Cattle-save-chrome tan.
3. Cattle-nonchrome tan.
4. Thru-the-blue.
5. Retan only.
6. No beamhouse tannery.
7. Shearlings tannery.

The primary criteria for categorization were the type or condition of animal hide processed, method of hair removal, type of tanning agent used, and extent of finishing performed. Plant size, age, and location, wastewater characteristics, and water usage were also considered.

Currently, wastewater from about 90 percent of the tanneries, accounting for approximately 80 percent of tannery industry production, is discharged to municipal systems.

It is concluded that leather tanning and finishing wastes dischared into properly designed and well operated publicly owned treatment works can be effectively removed. It is further concluded that municipal ordinances in cities with tanneries address most pollutants found in tannery wastewater and specify acceptable influent quality to be compatible with municipal treatment system processes and facilities.

It is concluded that sulfides and ammonia are the only incompatible constituents in tannery wastewater being discharged to publicly owned treatment works.

It is further concluded that technology is available and in used to achieve the removal of sulfide from tannery wastewater. There is no pretreatment technology practicable or in use to remove ammonia by the industry. The estimated capital cost of achieving sulfide removal by tanneries discharging to municipal systems is $7.3 million. Total annual cost (including depreciation, capital costs, operation, and maintenance) for this pretreatment limitation will increase unit costs for different tanneries by a cost varying from 5.6 cents to 76 cents per raw material hide for the cattlehide tanners in the industry and from 1.6 cents to 11 cents per skin for other segments of the industry. Tannery size will influence the specific plant cost within each of these ranges.

SECTION II

RECOMMENDATIONS

No specific numerical wastewater pretreatment standards are being recommended at this time. However, to avoid confusion, the terminology of "draft recommended limitations" or "pretreatment standards" has been used only to be consistent with the language of the Act to represent in draft form conclusions of the technical study regarding effluent levels achievable for discharge to a publicly owned treatment works.

SECTION III

INTRODUCTION

PURPOSE AND AUTHORITY

Section 307(b) of the Federal Water Pollution Control Act Amendments of 1972 (the Act) requires the Administrator to promulgate pretreatment standards for pollutants introduced into publicly owned treatment works. Section 307(c) of the Act requires the Administrator to establish pretreatment standards for new sources. The regulations proposed herein set forth pretreatment standards for existing sources pursuant to Sections 307(b) and 307(c) of the Act for the Leather Tanning and Finishing point source category.

This document is the first of three successive development documents that together normally comprise a single and complete point source category development document. This first document addresses only pretreatment in terms of limitations, standards, technology, and cost. This document is complete in addressing the industry description and trends, industry categorization, water use and raw wastewater characteristics, and pollutant parameters.

The second and third documents will address the requirements of the Act as set forth in Sections 304(b), 301(b), and 306 regarding the application of the best practicable control technology currently available by July 1, 1977, the best available technology economically achievable by July 1, 1983, and the establishment of Federal standards of performance for the Leather Tanning and Finishing point source category.

SUMMARY OF METHODS USED FOR DEVELOPMENT OF THE PRETREATMENT STANDARDS

The pretreatment standards set forth herein were developed in the following manner. The original development document (1974) and selected sections of the appendices to that document were acquired. The organization that prepared the original "draft" document was included on the current study team so that the benefit of their experience could be obtained and the incorporation of existing data and information on the tanning industry would be facilitated. The point source category was first studied for the purpose of determining whether separate limitations and standards may be appropriate for different segments within the point source category. This analysis included a determination of whether differences in raw material used, product produced, manufacturing process employed, equipment, age, size, wastewater constituents, and other factors may require development of separate effluent limitations and standards for different segments of the point source category. The raw waste characteristics for each segment were identified and used in this analysis. The analysis included consideration of: 1) the sources and volume of water used in the processes employed and the sources of pollutants and wastewaters in the plant, and 2) the constituents (including thermal) of all wastewaters, including toxic constituents and other constituents which produce taste, odor, or color in water or aquatic organisms. The constituents of wastewaters which should be considered for pretreatment standards, effluent limitations guidelines, and standards of performance were identified (see Section VI).

The full range of control and treatment technology existing within the point source category was identified. This included identification of each distinct control and treatment technology, including an identification in terms of the amounts of constituents (including thermal) and the chemical, physical, and biological characteristics of pollutants, and of the effluent level resulting from the application of each of the treatment and control technologies. The problems, limitations, and reliability of each treatment and control technology and the required implementation time were also identified. In addition, the nonwater quality environmental impacts, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste and noise were also identified. The energy requirements of each control and treatment technology was identified as well as the cost of the application of such technology.

In assessing treatment and control technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent quality achieved, equipment and facilities involved, the processes employed, the engineering aspects of the application of various types of control techniques, process changes, nonwater quality environmental impacts (including energy requirements) and other factors.

The specific data sources used to characterize the industry, the wastewater characteristics, and the industry practices with regard to wastewater generation and disposal include the following:

1. One-page surveys and detailed questionnaires were distributed to about 301 addresses of tanneries and finishers through the Tanners' Council of America to obtain information on specific plant situations. Survey responses were received from 114 tanneries. Questionnaires were returned by 89 tanneries.
2. Telephone contacts with municipalities were made to collect information on city ordinance wastewater limitations, reasons for limitations, wastewater problems experienced, and plans for dealing with the problems. Supplementary wastewater data for local tanneries and municipal performance data were also requested.
3. Information on plant operations, sites, practices, processes, equipment, management concerns and attitudes, and wastewater and production data was collected during field visits to 35 tanneries. This information was used to complement other data sources.
4. Wastewater sampling trips of two or three days were made to 14 tanneries. The sample of tanneries visited and/or sampled included facilities representative of most situations and operations found in the industry. Tanneries of different size and age of physical plant were observed, and tanneries in both large urban and in rural areas were visited.
5. NDPES permit data and background information on a number of tanneries were obtained from EPA regional offices. Permits included information on the tannery and waste treatment facilities and the discharge standards and schedule for compliance being set at the present time.
6. Engineering studies and reports were received on waste treatment facilities for several tanneries. These reports included dimensions and descriptions of the facilities, operating practices, data on wastewater quality and quantity, waste treatment design basis and criteria, treatment system problems, and cost estimates for wastewater control and treatment facilities.

7. Contacts were also made with state pollution control offices to request available data and information on tannery wastewater problems and plans for dealing with these problems.

GENERAL DESCRIPTION OF THE INDUSTRY

Leather tanning and finishing plants purchase hides and skins and manufacture leather for shoes, garments, upholstery, luggage, gloves, handbags, sporting goods, and a variety of other applications. Cattlehides, sheepskins and lambskins, and pigskins are the most numerous hide types used by U.S. tanneries in the manufacture of leather. Smaller quantities of hides and skins of horses, goats, deer, elk, and various other animals are also tanned each year in the U.S.

Some plants tan and finish a single species of animal hide. Other plants tan and finish a combination of animal hide types. Some plants have a single, very specialized end product such as lace leather or mechanical cushions for pianos. Other tanneries produce a variety of leather types for many consumer goods and industrial uses. The variety of products produced by the individual tannery influences the hide type and processing operations used by the tannery.

While many plants process from raw, green salted, or brined hides to finished leather, other plants do only a portion of the total process. Several tanneries purchase previously tanned hides and/or splits and perform only the retan, color, fatliquor and finishing processes. A number of tanneries purchase hides or skins which either do not require a complete beamhouse process, such as pigskins, or purchase hides or skins which have previously gone through the beamhouse, such as pickled cattlehides and pickled sheepskins. Another arrangement is used by a few tanners who have found it economically feasible to shift the high water use and strong pollutant beamhouse operation from the tannery location where stringent municipal effluent limitations exist to another location where either sufficient POTW capacity exists or where an effluent treatment system is readily implemented.

Tanneries are primarily located in four general areas of the U.S. There is a concentration in the New England states with clusters in the Mid-Atlantic states, the Midwest, and on the Pacific coast.

As indicated in Table III-1, tannery production from 1965 to 1974 trended downward. However, from 1975 data and

Table III-1. Production and Marketing Trends of the Leather Tanning and Finishing Industry

Year	Total Tanning Industry Production(2)	Total Industry Value of Shipments(1)	Cattle Hides(1) Net Exports	Leather(1) Imports	Exports(1)
	(1000 Equiv. Hides)	(Million Dollars)	(1000 Hides)	($1,000)	($1,000)
1965	32,697	857	13,019	66,998	39,474
1966	32,252	940	13,984	74,996	41,583
1967	30,861	870	11,634	68,045	42,321
1968	31,884	878	12,359	81,429	45,324
1969	28,388	854	14,513	85,805	41,586
1970	25,941	794	14,844	87,384	36,736
1971	25,267	838	15,694	83,273	42,832
1972	24,661	1060	17,292	138,795	66,706
1973	21,062	1082	16,177	127,381	82,914
1974	19,998	980	17,924	124,513	102,116
1975	21,894	1105	20,329	87,953	140,497
1976*	23,000	1200			

*Estimated

Source: (1) U.S. Department of Commerce

(2) Tanners Council of America, Inc.

projected 1976 data, total industry production, both in equivalent number of hides and in total dollar value, appears to be increasing.

In the 1960's and early 1970's, from an economic standpoint the domestic leather tanning and finishing industry felt a squeeze due to: 1) greater foreign demand for cattlehide which caused an increase in cost of cattlehides; and 2) competition from foreign countries in the finished leather products market[1].

As shown in Table III-1, cattlehide exports increased from 1965 to 1975. There was also a general increase in leather import dollar value. However, the dollar value of leather exports also increased. Finally, in 1975, leather exports exceeded leather imports as measured in dollars.

Increase in leather production, increase in dollar value of total industry production of leather, and increase in dollar value of leather for export are three indications of a viable U.S. leather tanning and finishing industry. Management and owners of tanneries express confidence in the industry both verbally and by continuing capital investments in tanneries.

STANDARD MANUFACTURING PROCESSES

Tanning is a term used generally to describe all the numerous processing steps involved in converting animal skins or hides into leather. Skin is composed of epidermal and dermal layers with flesh attached to the inner or dermal layer. The dermis constitutes the leather-making portion of the skins or hides, and consists mainly of the protein collagen. Tanning is essentially the reaction of collagen fibers with tannin, chromium, alum, or other tanning agents.

The practice of preserving skins began before recorded history and grew into a finely developed art. In recent times the art of tanning has been modified by the application of scientific principles and aided by the use of scientific instruments. 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 concentration and/or temperature may be increased to decrease the processing period. Tanners vary process conditions based on individual and collective experience to produce various finished products. Therefore, there are some variations in processing techniques, especially in the use of chemicals and in other details (even between two tanners producing the same finished product), to produce a product of consistent quality.

The variations in processing techniques used to convert different types of animal skins to tanned and finished leather are contributing factors in wastewater generation in the leather tanning and finishing industry. These variations are recognized in the classification system used to describe the industry.

For purposes of characterizing waste loads, the following standard tannery processes were used: beamhouse, tanyard, retan, color, fatliquor, and finishing. These processes are shown schematically in Figure III-1. Chemicals such as lime, sodium sulfide, sodium sulfhydrate, ammonium salts, enzymes, basic chromium sulfates, vegetable tanning extracts and compounds, mineral acids, alum, natural and synthetic fatliquors, acid dyes, some solvent coatings, and sodium chloride are employed within the various processes.

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 variation of processes used among plants. With this approach, waste loads and effluent requirements can be more readily described.

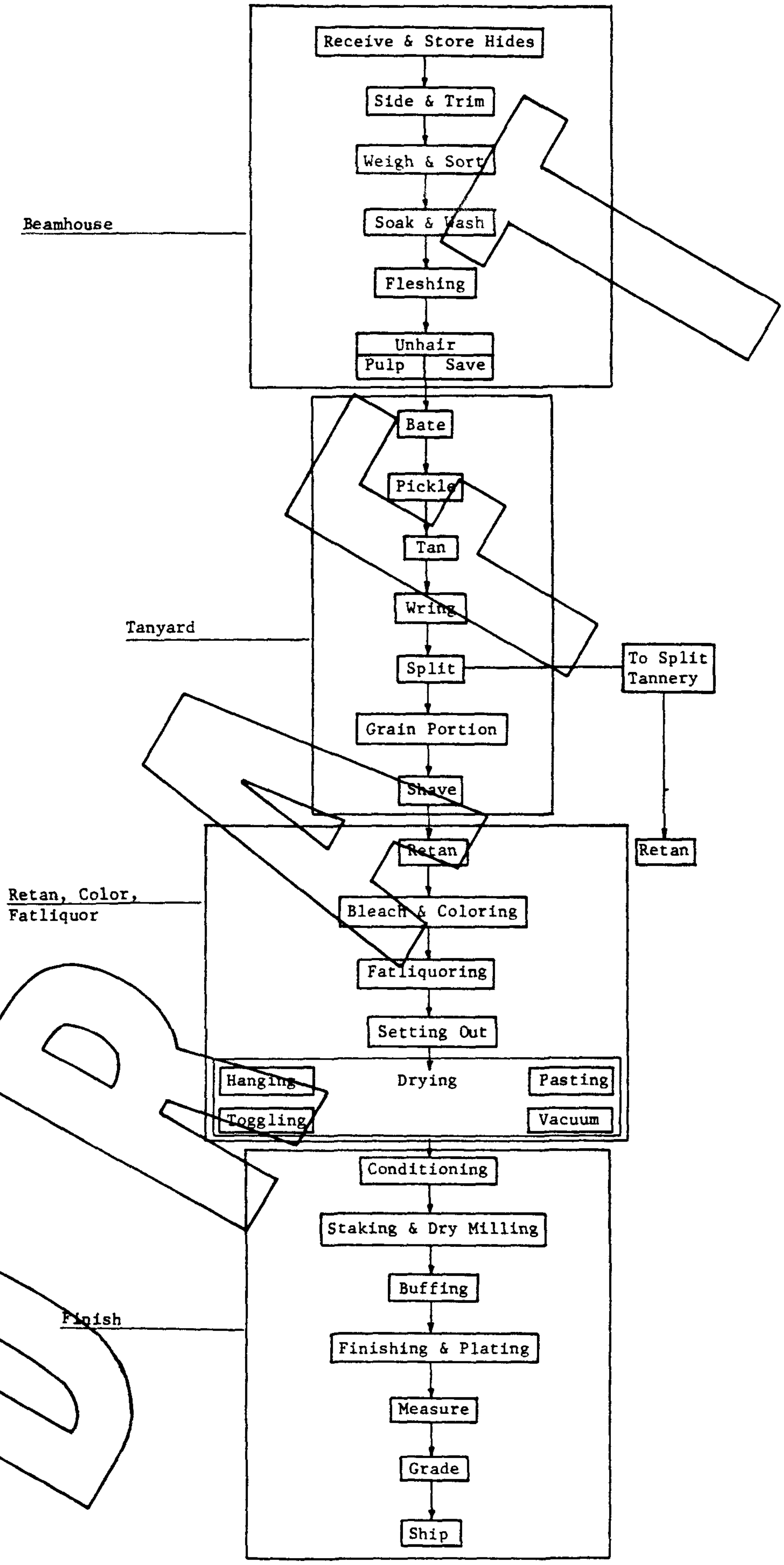
The discussion and description of tannery processes which follow are based upon the three major hide and skin types produced in the U.S.: cattlehides, sheepskins, and pigskins. The processes and sub-processes discussed represent an inventory of those most typical of the entire industry.

Cattlehide Tannery Processes

Much of the following process description of a typical cattlehide tannery was drawn in detail from the book Leather Facts, published by the New England Tanners Club[2].

Three processes in a typical cattlehide tannery contribute waste loads:

Figure III-1. GENERAL PROCESS FLOWSHEET FOR LEATHER TANNING AND FINISHING INDUSTRY



1. Beamhouse
2. Tanyard
3. Retan, color, fatliquor, finishing

Detailed descriptions of the process and sub-process operations follow.

Beamhouse Process:

1. Receiving--Nearly all cattlehides received at tanneries are either green salted or brine cured hides, with the brine cured hides predominating. In a few isolated cases where transit time is short, fresh green hides without prior curing are sent directly from a meat packer to a tannery for immediate processing.

   Green hides, after trimming and grading, are cured at the packinghouse 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 five to six feet high results. A heavy layer of salt is placed over the top layer of hides. The natural fluids from the hides dissolve a portion of the salt to form a brine. In this process, salt is absorbed and by diffusion and osmosis causes 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 plant, size of shipments, and the method of shipment.

   Brined hides are prepared at the packing plant 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 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 take 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--Normally the tanner receives and stores hides in a large, cool, well ventilated area designed to keep the hides at the moisture content as received.

3. Siding and Trimming--A typical first step in preparing hides for processing consists of opening the bundles and trimming off the heads, long shanks, and other perimeter areas which do not make good leather. The hides then may be cut lengthwise along the backbone, head to tail, to make two sides. Sometimes hides are halved or sided after unhairing or tanning. A number of sides are then gathered to form a pack which is identified as to size, weight, type of skin, and any other information that will be important in later processing. Trimmings are often collected for shipment to glue or other by-product manufacturers.

4. Soaking and Washing--The sides are soaked in vats (with or without paddles), drums, or hide processors (concrete mixers with special linings) for 8 to 20 hours to restore moisture which the hides have lost as a result of the curing process. The hides gradually absorb water, becoming softer and cleaner. After soaking the skins are washed to remove dirt, salt, blood, manure, and non-fibrous proteins. 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 unhairing, after bating, after tanning, and prior to and following coloring.

5. Fleshing--Fleshing is a mechanical operation which rids the hides of excess flesh, fat, and muscle found on the inside or flesh side of the skins. It is done on a fleshing machine, in which the hide is carried through rollers 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.

   Many hides are fleshed at the packing plant 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. However, on-site rendering of fleshings produces a low volume yet extremely concentrated wastewater stream ("stick liquor").

6. Unhairing--Commonly used unhairing processes employ calcium hydroxide and sodium sulfide. The chemicals 1) destroy the hair or attack the hair roots, 2) loosen the epidermis, and 3) remove certain soluble skin proteins.

   Fleshed hides are placed in paddle vats containing water and the depilatory chemicals. The concentration of chemicals, water temperature, and amount of agitation directly affect the rate at which unhairing proceeds. In a pulp or brine hair operation higher concentrations and temperatures result in very rapid hair removal with the entire hair being dissolved in a few hours. If it is desired to save the hair for its commercial value, a longer procedure using weaker solutions and lower temperatures is employed. This results, after up to two to four days in an attack of the hair roots only, and the loosened hair can be collected, washed, dried, and sold.

   In cases where the chemical treatment alone does not remove all the hair or hair roots, the process can be completed on an unhairing machine.

This is very similar to a fleshing machine except the cylinder blades are blunt and produce a rubbing action rather than cutting.

The lime and sulfide chemicals used in unhairing produce a concentrated alkaline solution. The hide fibers under such conditions acquire a considerable affinity for water. As a result the fibers absorb large amounts of moisture which makes them swell. An unhaired skin in the lime-sulfide state is about twice its normal thickness, a condition which tanners call alkaline swelling.

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

7. Bating--The first phase of the bating process is termed deliming. Alkaline chemicals used in the unhairing process are present in fairly large amounts and must be removed. Deliming largely eliminates the lime and alkaline chemicals present. The hides are washed in large cylindrical drums. Salts of ammonium sulfate or ammonium chloride are added to convert the residual lime into soluble compounds which can later be washed free of the system. As this process takes place, some of the excessive alkaline swelling begins to disappear, and the skins start to return to a more normal thickness.

The deliming chemicals also adjust the pH conditions to the proper point for receiving the bate. Bates are enzymes similar to those found in the digestive systems of animals. These enzymes facilitate separation of the collagen protein fibers through hydrolytic destruction of peptide bonds which cross-link chains of amino acids. Bating also attacks and destroys most of the remaining undesirable constituents of the skin such as hair roots and pigments. Removal of these materials imparts a softer, less harsh feeling to the grain surface and gives it a cleaner appearance.

As in unhairing, the amount of bating material, temperature, and length of time are critical. Commercial processes vary from a few hours to overnight depending on the nature of the skins being handled.

Modern bates are actually mixtures of chemical deliming agents and various enzymes, permitting both phases of this process to be conducted simultaneously.

At the conclusion of bating, the hides are thoroughly washed to remove all of the substances which this process has loosened or dissolved.

8. Pickling--Pickling places the hides in an acid environment ready to accept the tanning materials. This is necessary particularly in chrome tanning to prevent precipitation of chromium salts, as chrome tanning agents are not soluble under alkaline conditions. Sulfuric acid is most commonly used for this purpose. Common salt or brine must first be added to the system. If acid were added alone, excessive acid swelling (similar to alkaline swelling) would develop, resulting in production of inferior leather or destruction of the hide substance into an unstructured gelatinous mass which cannot be tanned. Controlled acid swelling, however, further aids the separation of collagen protein fibers which facilitates further complexing by the tanning agent (i.e., trivalent chrome) and more complete stabilization.

   Only a few hours are necessary for the salt and acid to penetrate completely.

   The pickling operation is a preserving technique in its own right. Skins can be kept in this state for extended periods of time. Pickling is always done before chrome tanning and may be done before vegetable tanning.

Tanyard Process:

1. Tanning--The primary function of any tanning agent is to convert the raw collagen fibers of the hide into a stable product which is

no longer susceptable to putrefaction or rotting. In addition, these materials significantly improve many of the mechanical properties of the hide--for example, its dimensional stability, abrasion resistance, resistance to chemicals and to heat, (i.e., "boil test") the ability to flex innumerable times without breaking, the ability to endure repeated cycles of wetting and drying, etc.

Chrome, vegetable, alum, and syntans are the principal tanning agents used in the U.S. with chrome and vegetable predominating.

Vegetable tanning, the older process, is performed in a solution containing plant extracts. This method is usually used for the heavy leathers such as sole leather, mechanical leather, and saddle leather. Vegetable tanning is usually done in vats, primarily because of longer process times.

Shoe upper leathers and other lighter leathers are usually chrome tanned by immersion in a bath containing mixtures of basic chromium sulfate. Chrome tanning usually takes place in drums.

Chrome tanning is performed because it can be accomplished in a shorter time (four to six hours) and because it produces a leather that combines to best advantage most of the chemical and physical properties sought after for the majority of leather uses. The chemical state of the tanning agent as well as condition of the hides and interior of the drum are important to the thorough penetration of the chrome into the hide substance to complex the separated collagen protein fibers. Sodium bicarbonate and formic acid (masking agent) are added to increase the affinity of the hide protein for the chrome.

The older, commonly used, and more traditional method of tanning, known as the "two-bath" method, entailed the use of hexavalent chromium, which is first penetrated into the hide (first bath), and then a reducing agent such as thiosulfate is introduced to "blue" the hides (second bath) by <u>in situ</u> chemical reduction of chromium to the trivalent state which then complexes the proteins. Very few tanners still use this method in light of the dangers of handling hexavalent chromium which is very toxic and the reduced processing time and chemical cost in using trivalent chromium. Some tanners still purchase hexavalent chromium (bichromate, dichromate) and reduce it to trivalent chromium on site with dextrose or molasses and acid, prior to use in the tanning process. This is done primarily because of cost differentials between hexavalent and trivalent chromium available from chemical manufacturers in certain areas.

In either case, the chemically reducing environment provided by the organic content of leather tanning wastewaters serves to reduce to trace amounts any residual hexavalent chromium.

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.

2. Wringing--Wringing removes excess moisture from the blue hide in preparation for splitting. The hides are fed through a machine with two large rollers very similar to a clothes wringer.

3. Splitting and Shaving--Splitting adjusts the thickness of the hide to that required for the finished product. Thickness of all hides varies, age being an important factor. Different parts of the skin will also be of various thicknesses. Splitting yields a grain portion of uniform thickness and a split (or flesh side). The split layer can be processed separately or sent to split tanneries to be made into suede types of leather.

   Shaving is done on the grain portion to clean any remaining evidence of fleshy matter from any areas which were not thick enough to come into contact with the splitting knife. The shaving machine can also be used to further level the skin to exact specifications.

Retan, Color, Fatliquor, Finishing Process:

1. Retan--Since most tanners do not have either the equipment or the low-cost labor to have multiple beamhouse and tanyard formulae for the various finished leather products, virtually all hides receive essentially identical processing through the blue or tanned state. Therefore, retanning is done principally to impart characteristics to the finished leather which it would lack if tanning were carried out in only one step. The more common tanning agents for this purpose are vegetable extracts and syntans.

   Vegetable extracts help in retanning to minimize any variation that may exist between different parts of the chrome tanned hide.

   Syntans are man-made chemicals, used extensively in the manufacture of the softer side leathers. Because of their pronounced bleaching effect on the bluish-green color of chrome tannage, they are very useful in making white or pastel shades of leather.

   Retanning is usually done in a drum and is usually completed in one or two hours.

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. Two important factors are: 1) skin variability (such as varying pigmentation), and 2) penetration (which refers to the depth to which the coloring material penetrates into the leather).

   Typical dyestuffs are aniline based, and combine with the skin fibers to form an insoluble compound. pH control is used to vary the affinity of the dye for the leather fibers which in turn affects resulting shades, degree of penetration, etc.

4. Fatliquoring--Fatliquoring is a process by which the fibers are lubricated so that after drying they will be capable of sliding over one another. Natural oils are lost in the beamhouse and tanyard processes. Oils and related fatty substances in fatliquors replace those oils. Chemical emulsifiers are added to the fatliquor ingredients to permit dispersion in water. Fatliquoring requires approximately one hour. Use of differing amounts of oil permits the tanner to achieve varying degrees of firmness in the final product.

   Fat liquors typically and predominantly are either of animal or vegetable origin, or are synthetics made of modified mineral based oils. Straight-chain aliphatic mineral oils, are used by comparison in very small quantities for specialty heavy mechanical leathers which are produced in the stripping process.

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

5. Finishing--Finishing operations such as surface (grain side) dyeing 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. Solvent based coatings are used only for special high luster finishes. Use of these solvent based coatings has been curtailed largely due to the difficulty in handling them and the fire hazard involved.

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

   A. Setting Out--Setting out smooths and stretches the skin, while compressing and squeezing out excess moisture.

   B. Drying--Drying is accomplished by four different methods.
      1) Hanging--the hide is draped over a horizontal shaft which is usually passed through a large drying oven.

2) Toggling--the skins are dryed in a stretched position on frames. The frames are slid into channels in a drying oven.
3) Pasting--the skins are pasted onto plates which are then transported into a drying oven.
4) Vacuum--the hides are smoothed out on a heated steel plate and covered by a perforated belt or cloth-covered steel plate. A vacuum is pulled which extracts water from the leather. Unlike the first three processes which take four to seven hours per skin, this method requires only three to nine minutes. This method is not widely used due to shrinkage.

C. <u>Conditioning</u>--A mist is sprayed on the hides, which are then piled on a table, wrapped in a watertight cover, and kept overnight to permit uniform moisture distribution in the leather.

D. <u>Staking and Dry Milling</u>--Staking is done on automatic machines which stretch and flex the leather to make it soft and pliable. Dry milling consists of tumbling the hides in a large drum.

E. <u>Buffing</u>--Buffing smoothes or "corrects" irregularities in the grain surface by mechanical sanding.

F. <u>Finishing</u>--A number of finishes may be applied depending on the end use and type of hide. Various coating materials, both water-base and solvent-base, are used to provide abrasion and stain resistance and to enhance color.

G. <u>Plating</u>--Plating is the final processing step which influences the appearance and feel of leather. It smoothes the surface of the coating materials while bonding them firmly to the grain. The finishing and plating operations are carried out in conjunction with each other over a period of four to five days. Hides may also be embossed (stamped with a particular pattern).

H. <u>Measuring</u>--The hide area is determined.

I. <u>Grading</u>--Grading determines the quality of the finished product. Leather is graded for temper, uniformity of color and thickness, and the extent of any surface defects.

Sheepskin Tannery Process

The two major processes are:

1. Tanyard
2. Retan, Color, Fatliquor, Finishing

These processes and the subprocesses which take place during manufacturing are described as follows:

Tanyard Process:

1. Receiving--Sheepskins are received at United States tanneries from both domestic and foreign sources. Imported skins are generally pickled skins. Pickled skins are preserved for shipment and storage by immersion in a solution of brine and acid. Excess solution is drained prior to handling. The skins are normally tied in bundles of one dozen skins. These skins have had the wool removed at the packing-house or wool-pullery before being 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, except for fleshing. Shearling skins are cured in a salt brine only.

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 degrees C (86 degrees F) to avoid deterioration[1]. Biocides, such as chlorinated phenolics, are used to retard bacterial action and increase storage time.

3. Fleshing--Skins from storage are taken from the 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 rollers and across rotating spiral blades which remove the flesh. Fleshings and trimmings are normally collected and disposed of as solid waste.

4. Degreasing--Skins are placed in drums, washed, and soaked, after which solvent or detergent is added 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 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 chrome containing solid waste.

Retan, Color, Fatliquor, Finishing Process:

1. Retan--Retanning is performed in a manner similar to the cattlehide retanning operation.

2. Coloring--Skins to be colored are immersed in a dye solution in drums. Synthetic dyes are generally used, and some bleaching may be done prior to coloring of shearlings.

3. Fatliquoring--Fatliquoring 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.

4. Finishing--There are a number of operations which follow the coloring and fatliquoring 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 wastewater system.

Pigskin Tannery Process

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 tanyard sub-process. The two major processes are:

1. Tanyard
2. Color, Fatliquor, Finishing

Tanyard 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 most 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 are 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 from the top of holding tanks to which the waste has been 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 purpose of this step 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 solution 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 major tanner of pigskin in this country is using only the chrome tanning process. Chrome tanning is conducted in the same drum used for pickling, using 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 to obtain the desired thickness. The split portion of the 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, Fatliquor, Finish 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 various oils to replace the natural oils of the skin lost in the tanning process.

3. Finishing--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 solid waste.

SECTION IV

INDUSTRY CATEGORIZATION

In developing effluent limitations guidelines, pretreatment standards, and standards of performance for the leather tanning industry, judgments are necessary as to whether limitations and standards are appropriate for different segments (subcategories) within the industry. To identify such subcategories the following factors were considered:

* Hide or skin type, i.e., cattlehide, shearling, pickled sheepskin, split, etc.
* Beamhouse operations
* Tanning agent, i.e., chrome, alum, vegetable
* Finishing operations including retanning
* Plant size
* Plant age and location
* Wastewater characteristics and treatability

After considering all of these factors it was concluded that the leather tanning industry consists of seven subcategories. Four of the subcategories comprise primarily the cattlehide to leather tannery segment of the industry; two of the subcategories comprise primarily that tannery segment with no beamhouse, that tan and finish only; and one subcategory comprises primarily the shearling (sheepskin tanned with hair on) tannery segment.

The subcategories are defined as follows:

1. Cattle-pulp-chrome--a tannery that primarily processes raw or cured cattle or cattle-like hide into finished leather, chemically dissolving the hide hair, and using chrome tanning and usually wet and dry finishing.
2. Cattle-save-chrome--a tannery that primarily processes raw or cured cattle or cattle-like hide into finished leather, loosening and removing at least a portion of the hide hair as a solid, and using chrome tanning and usually wet and dry finishing.
3. Cattle-nonchrome--a tannery that primarily processes raw or cured cattle or cattle-like hide into finished leather usually hair save, using less than 20 percent (by hide weight) chrome tanning, using instead vegetable, alum, syntans, oils, and other methods and their combinations for tanning, and usually wet and dry finishing.

4. Thru-the-blue--a tannery that primarily processes raw or cured cattle or cattle-like hide through the blue tanned state only, with no retanning or finishing operations, using chrome tanning.
5. Retan only--a tannery that primarily processes previously tanned hides and/or skins (including splits) into finished leather, the major wet process consisting of retanning, coloring, and fatliquoring.
6. No beamhouse (NB) tannery--a tannery that primarily processes hides and/or skins, with the hair previously removed, into finished leather using either chrome or nonchrome tanning methods, primarily includes pickled sheepskin and cattlehides, and pigskins.
7. Shearlings--a tannery that primarily processes raw or cured sheep or sheep-like skins, with the wool or hair retained on the hide, into finished leather using chrome or nonchrome tanning; or, a wool pullery, a plant that processes hair-on raw or cured sheep or sheep-like skin by first removing the wool and then pickling the skin for use by a sheepskin tannery (subcategory 6).

CLASSIFICATION SYSTEM

The leather tanning industry, Standard Industrial Classification No. 3111, does not consist of a homogenous grouping of plants with similar operations, practices, and procedures. Wide variations in hide or skin types processed, degree of finishing, and in-plant processes exist to such a degree that a classification of the various plant types was made for purposes of analysis. In a procedure similar to that in the earlier development document for this industry[1], four digits were used to classify the industry into distinctive groups of plants. As shown in Table IV-1, the four-digit numbers relate information on type of skin or hide, operations in the beamhouse, tanning agent used, and the use of retan, color, fatliquor, and finishing steps.

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

1111--Cattlehide (including calfskin), hair is pulped, chrome tanning process used, sides finished.

Table IV-1. Classification System (3111. abcd)

Skin or Hide Type		Beamhouse Operation		Tanning Process		Retan, Color, Fatliquor, Finishing	
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.	Chrome and Other	5.	Skins
6.		6.	Hide Curing	6.	Various	6.	Various
7.		7.	Pulp & Save	7.		7.	
8.		8.	Various	8.		8.	
9.	Other	9.	Other & Unknown	9.	Other & Unknown	9.	Other
0.	Various	0.	None	0.	None	0.	None

NOTES:

1) Beamhouse operation classification #3 (hair previously removed) and #0 (none) differ due to survey reporting and potential fleshing procedures (primarily sheep).

2) Tanning process classification #5 (chrome and other) requires at least 20 percent chrome tanning to be so classified.

3) Retan, color, fatliquor, finishing classification #1 (sides) includes sides and splits where the number of splits processed is not greater than the number of sides processed, in classification #3 (sides and splits), the number of splits processed is greater than the number of sides.

4) Various classifications are combinations of other operations or processes listed in the same column.

1211--Same as 1111 except hair is saved as a by-product.

1221--Same as 1211 except vegetable tanning process used.

1110--Same as 1111 except no retan, color, fatliquor, or finishing is done (tanning to blue stage only).

1041--Cattlehide, no beamhouse, hide previously tanned prior to receipt of hides at a finishing facility (finishing operations only).

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.

3015--Sheepskin, no beamhouse, therefore hair removed, pickled sheepskin raw material, chrome tanning process used, skins finished.

3415--Sheep shearling, washed and fleshed, chrome tanning process used, skins finished.

SUBCATEGORIZATION SYSTEM

The tanning industry's present combinations of standard manufacturing operations are described by approximately 52 four-digit classification codes which are combinations from Table IV-1. As a first step in the categorization analysis, the classification codes were grouped by process similarity omitting those plants where a distinctly dominant process (i.e., classified as "various") was not observable. Ten industry groups resulted based on the differences in hide/skin type, beamhouse methods, tanning agent, and finishing operations. Based on similarity of raw waste loads (as measured by pollutant loading per unit weight of hide/skin processed), chromium use, and water use (as measured by volume of water per unit weight of hide/skin processed) the final number of subcategories was reduced to seven, and the mixed process plants assigned to the appropriate subcategory on the basis of dominant process. Table IV-2 shows the classification numbers and tannery descriptions included in the resulting subcategories. Four types of plants with codes of 0151, 1100, 3002, and 3115, are not categorized because of insufficient data. Table IV-3 shows the relationship between these subcategories and those in the original development document on tanneries[1].

Table IV-2. Categories of the Leather Tanning and Finishing Industry

1 Cattle, Pulp, Chrome

1111	Cattle	Pulp	Chrome	Sides
1113	Cattle	Pulp	Chrome	Sides & Splits
1151	Cattle	Pulp	Chrome & Other	Sides
1153	Cattle	Pulp	Chrome & Other	Sides & Splits
0116	Various	Pulp	Chrome	Various
0156	Various	Pulp	Chrome & Other	Various

2 Cattle, Save, Chrome

1211	Cattle	Save	Chrome	Sides
1213	Cattle	Save	Chrome	Sides & Splits
1251	Cattle	Save	Chrome & Other	Sides
1711	Cattle	Pulp & Save	Chrome	Sides
1751	Cattle	Pulp & Save	Chrome & Other	Sides
4215	Deer	Save	Chrome	Skins
0256	Various	Save	Chrome & Other	Various
0816	Various	Various	Chrome	Various
0756	Various	Pulp & Save	Chrome & Other	Various
0716	Various	Pulp & Save	Chrome	Various

3 Cattle Nonchrome

1221	Cattle	Save	Vegetable	Sides
1121	Cattle	Pulp	Vegetable	Sides
1131	Cattle	Pulp	Alum	Sides
1261	Cattle	Save	Various	Sides
1731	Cattle	Pulp & Save	Alum	Sides
4125	Deer	Pulp	Vegetable	Skins
1163	Cattle	Pulp	Various	Sides & Splits

4 Thru-The-Blue

1110	Cattle	Pulp	Chrome	None

5 Retan Only

1041	Cattle	None	Previously Tanned	Sides
1342	Cattle	Hair Previously Removed	Previously Tanned	Splits
1042	Cattle	None	Previously Tanned	Splits
1043	Cattle	None	Previously Tanned	Sides & Splits
0016	Various	None	Chrome	Various

6 No Beamhouse Tannery

1013	Cattle	None	Chrome	Sides & Splits
1313	Cattle	Hair Previously Removed	Chrome	Sides & Splits
1059	Cattle	None	Chrome & Other	Other
1012	Cattle	None	Chrome	Splits
1051	Cattle	None	Chrome & Other	Sides
1062	Cattle	None	Various	Splits
1023	Cattle	None	Vegetable	Sides & Splits
1011	Cattle	None	Chrome	Sides
2315	Pig	Hair Previously Removed	Chrome	Skins
3015	Sheep	None	Chrome	Skins
3355	Sheep	Hair Previously Removed	Chrome & Other	Skins
0435	Various	Hair Retained	Alum	Skins
3395	Sheep	Hair Previously Removed	Other & Unknown	Skins
3055	Sheep	None	Chrome & Other	Skins
3052	Sheep	None	Chrome & Other	Splits
0855	Various	Various	Chrome & Other	Skins

7 Shearlings

3415	Sheep	Hair Retained	Chrome	Skins
3455	Sheep	Hair Retained	Chrome & Other	Skins
3500	Sheep	Wool Pullery	None	None

Table IV-3. Category Comparison by Principal Processes

Present Document Category	EPA Development Document March 1974 Category
1. Cattle, Pulp, Chrome	1
2. Cattle, Save, Chrome	2
3. Cattle, Nonchrome	3
4. Thru-the-Blue	6
5. Retan Only	4
6. No Beamhouse	5
7. Shearlings	5

RATIONALE FOR CATEGORIZATION

Hide or Skin Type

The type of hide or skin processed in a leather tannery is a significant factor in subcategorizing the industry especially regarding the use of those processes for removal, recovery, or washing the hair on the hide/skin. The subcategories are based on the following hide/skin types:

1. Cattlehide or cattle-like hide--short hair, relatively heavy hides or skins. Deerskin, horsehide, cow bellies, and other similar hides are included in this group.
2. Sheep or sheep-like skins--long hair relatively light skins. Goatskin and other similar hides are included in this group.
3. Pig or pig-like skins--short or hairless relatively light skins. To be included in this group the skin must have little or no hair.

A differentiation in the plant groups based both on raw waste load (weight per unit weight of hide) and water usage (volume per unit weight of hide) is obtained due primarily to the method of hair removal (full pulping, semi-pulping, hair save) and the amount of hide washing required, which depends primarily on type of hide. Once the hair is removed during processing, raw waste generation and water usage on a unit production basis will tend to be similar regardless of hide or skin type.

Beamhouse Operations

The beamhouse operation in a leather tannery is a significant factor in subcategorization and is based on the following operational variations:

1. Pulp hair--hair is chemically dissolved and enters the liquid waste stream.
2. Save hair (and wool pullery)--hair (or wool) is chemically softened and is then removed mechanically. The majority of the bulk hair removed as a solid does not enter the liquid waste stream. Residual roots and fragments may enter the waste stream.

3. No beamhouse--the tannery receives its hides or skins with the hair previously removed; therefore has no beamhouse and generates no beamhouse-type waste stream. Included in this group are hides that require little or no hair removal such as pickled sheepskin or cattlehides and pigskin.

There is a substantial difference in water usage and raw waste pollutant content between a no-beamhouse tannery and one with a beamhouse. High water use and waste loadings are typical of beamhouse effluent. Subcategorization including this basis is thus substantiated.

Tanning Agent

The tanning agent is a significant factor in subcategorization of the leather tanning industry primarily from the standpoint of potential specific waste problems resulting from the use of the various tanning agents available to the industry. The subcategorization is based on the following tanning agents and methods used in the industry:

1. Chrome tanning--chromium salts are at least 20 percent (by weight of hide tanned with this agent) of the tannage used. Many plants in the industry use only this tanning method and most plants use primarily chrome.
2. Nonchrome tanning--less than 20 percent by weight of the hide is chrome tanned. Nonchrome tanning agents primarily include alum, vegetable extracts and synthetics.
3. Previously tanned--no tanning (only retanning) is carried out because the plant receives its hides in a fully tanned state.

Chrome tannery raw waste streams may contain chromium in the trivalent state. Hexavalent chromium has not been found in significant quantities in raw waste streams; only in trace amounts or not at all. Nonchrome tanning methods may generate a highly colored raw waste, but the raw waste and water usage are somewhat reduced from the chrome tannery. A leather tannery that only retans and finishes (using previously tanned hides) generates significantly lower raw BOD_5 in the waste stream and also has a lower water use per unit application.

Finishing Operations, Including Retanning

Finishing operations, with retanning included, are significant in the industry categorization only by presence or absence. Water usage and raw waste loadings in plants that only retan and finish are significantly less than for other categories. Plants that finish only (no retanning step) are not considered to be tanneries and were excluded from consideration in this study. Differences in waste generation between plants that tan but do not finish and those that tan and finish would be expected, but are not detectable due to limited data for the former and are overwhelmed by waste loading variations as reported by individual tanneries. Thus the subcategorization is substantiated, especially the specification of retan only subcategory, which is primarily wet finishing.

Plant Size

Plant size *per se* is not a factor in categorizing the industry. There is a wide range of size of plants in the various subcategories; however, the range in raw waste pollutant content from plants grouped by size was essentially equal for large and small plants. There are no other factors relevant to categorizing the industry that coincide with plant size. Thus a categorization that does not include size is substantiated.

Plant Age and Location

Plant age and location do not influence leather tanning processes or wastewater control practices such as to require consideration in the subcategorization. Most of the plants are quite old, but even processing equipment for newer plants is similar to, or identical with, equipment found in the older tanneries. There is no consistent difference in plant operations or wastewater generation associated with tannery age.

There is no discernible relationship between plant location and raw waste load. Wastewater generation and treatability were not found to vary with tannery location. Design principles and practices for waste water treatment consider climatic factors. Tannery location and hide source are not necessarily coincident. Hides are usually purchased on the basis of grade and source by the tanneries for specific final product applications. Tannery location and hide source are independent of one another with rare exceptions in the industry. Thus the categorization is further substantiated.

Wastewater Characteristics and Treatability

Industrial practices within the leather tanning industry are diverse and produce variable waste loads. It is possible to develop a rational division of the industry, however, on the basis of factors which group plants with similar raw waste characteristics. These raw wastes are amenable to the same treatment techniques. Thus waste characteristics and treatability substantiate the subcategorization.

The primary wastewater characteristic used as the basis in categorizing the industry is five-day biochemical oxygen demand (BOD5) in units per 1000 units hide weight--kg BOD5/1000 kg hide (lb BOD5/1000 lb hide). BOD5 provides the best measure of plant operation and treatment effectiveness among the wastewater parameters measured, and more data is available for BOD5 than for any other parameter. Total suspended solids data serve to substantiate the conclusions developed from BOD5 in categorizing the industry.

The major plant waste load is organic and biodegradable; BOD5, which is a measure of biodegradability, is the best measure of this type of loading entering a waste stream from a plant. Furthermore, because secondary waste treatment is a biological process, BOD5 also provides a useful measure of the treatability of the waste and the effectiveness of the treatment process. Chemical oxygen demand (COD) measures total organic content and some inorganic content. COD is a good indicator of change, but does not relate directly to biodegradation, and thus does not indicate the demand on a biological treatment process or on a stream.

As described in more detail in Section V, differences exist in the average BOD5 loads for raw wastes for the seven subcategories of the leather tanning industry. As defined earlier, the groupings by plant type are substantiated as subcategories on the basis of waste load. As described earlier, other raw waste parameters significant in subcategorization are sulfides and total chromium. Chromium is recognized as an important constituent of tannery wastewater, hence the distinction between "chrome" and "nonchrome" in the subcategorization. Sulfides originate from chemicals used in the beamhouse unhairing operations and from residues of these chemicals in the hides. The requirement to remove sulfides from wastewater as recommended in this report impacts only those tanneries using the unhairing chemicals and these plants fit only in certain categories.

Table IV-4 presents a summary of average plant operating parameters for each subcategory, the parameters include production, wastewater flow, BOD5, total chromium, and sulfides loading in the raw waste.

A number of additional waste load parameters were also considered. Among these were nitrites and nitrates, Kjeldahl nitrogen, ammonia, total dissolved solids, total volatile solids, oil and grease, chlorides, total alkalinity, and phenols. In each case, data were insufficient to justify categorizing on the basis of the specified parameters; however, for the most part, these parameters confirm the BOD5 raw waste based subcategorization. With the exception of chromium and sulfide, wastewaters from tanneries contain the same constituents and are amenable to the same biological treatment techniques. Judging from secondary waste treatment results, tannery effluent does not impair secondary waste treatment effectiveness, and in fact the waste constituents of tannery waste are removed by such treatment processes. Tannery wastewater constituents and flow patterns are primary determinants of waste treatability. Within the tannery industry, the variations that do occur in either factor are consistent throughout the industry or the differences are reflected in the categorization, thereby confirming the categorization.

It was anticipated that geographical location, and hence climate, might affect the treatability of the waste to some degree. Climate has occasionally influenced the kind of secondary waste treatment used, but has not had an influence on the ultimate treatability of the waste or the treatment effectiveness, given careful operation and maintenance; in fact as mentioned above, some of the "best" secondary treatment systems (treating primarily tannery wastes) are in the more severe northern climates.

Table IV-[illegible]. Production, Wastewater Flow, and Raw Waste Loading by Subcategory

	Subcategory 1 Cattle Pulp-Chrome	Subcategory 2 Cattle Save-Chrome	Subcategory 3 Cattle Non-Chrome	Subcategory 4 Thru-the-Blue	Subcategory 5 Retan Only	Subcategory 6 NB Tannery	Subcategory Shearlings
Average Production							
Hides/Day	1750	1290	710	2530	2620	2980	1830
Kg/Day	39,000	28,600	20,000	81,600	36,500	13,600	9,100
Wastewater Flow							
CuM/Kg	6.038	0.045	0.038	0.02	0.014	0.027	0.116
Average Raw Waste BOD5							
Kg/100 Kg	59.2	60	42	126	10.2	26.2	75
Average Raw Waste Chromium Total							
Kg/100 Kg	3.15	2.4	0.53	6.3	1.3	1.1	3.4
Average Raw Waste Sulfide							
Kg/1000 Kg	2.6	2.7	2.6	7.6	<0.1	<0.1	<0.1

SECTION V

WATER USE AND WASTE CHARACTERIZATION

WASTEWATER CHARACTERISTICS

Water is an essential input and it is used in large quantities in the leather tanning and finishing industry. Water is used as a primary input material to clean, prepare, or condition hides/skins in some tannery processes, it is the media for carrying out other processes especially those involving reactions of chemicals with the hides, it is the carrier of other materials in tannery processes such as dyes and pigments in coloring, and it is used to clean tannery facilities and equipment. Wastewater with a material waste load originates from every wet process in a tannery. There is usually an insignificant amount of effluent from the dry finishing operations.

Wastewater from leather tanneries contains soluble and suspended organic matter including grease and oils, solids, inorganic materials such as salt, chromium salts, sulfide ammonia, other processing chemicals, small quantities of the nutrient pollutants, and a coliform count, in some cases. These pollutants enter the waste stream from the tannery operations as proteinaceous matter, hair, tissue, unfixed chemicals, tanning agents and extracts, dyes, pigments, dirt, grit, and manure.

Raw Waste Characteristics

The raw waste characteristics of the wastewater as reported in this section for each subcategory of the leather tanning industry are based on data collected from the various sources described in Section III and on the wastewater sampling program conducted during the course of this study. Raw waste is defined as the total plant wastewater available for sampling at the first access point in the plant. This is typically a catch basin or wet well, frequently including an integral screening device. Thus the raw waste characteristics reflect whatever pollutant loading reduction occurs in screening, which is usually very little.

The primary parameters used to characterize the raw waste are flow, BOD5, total suspended solids, oil and grease, total chromium, and sulfide. Other pollutant parameters, including solids and nutrients as described in Section VI, are also reported where available. These characteristics, other than flow, are expressed in units of weight per 1000 units of production as defined as the weight of raw material (hide/skin). The number of hides and average weight of hides during summer and winter as reported by the tanneries were used to compute a production level in weight of hides per operating day. The outflow of pollutants was then related to this production level on a unit weight per 1000 units weight basis for presentation as the raw waste characteristics. Flow of wastewater was related as the ratio of total volume per operating day to production level to derive a volume-per-unit-weight-of-production figure also as reported in the raw waste characteristics.

The production level based on weight of raw material is subject to variations both in average weight per hide/skin and in the actual number of hides processed on a given day for which wastewater data are available. The mix by type of raw material hides and the variable amounts of dirt, manure, salt, hair, flesh, etc., attached to the hides contributed substantially to variations in production level. These same factors can influence the raw waste loading. Thus, when the actual number of hides and/or the weight of input raw material is known concurrent with raw waste data, the raw waste characteristics should be representative of a specific tannery wastewater situation. The use of pollutant weight per 1000 units of raw material weight is the basis to be used in presenting the raw waste characteristics.

Since the data collection process for this study had as its goal the determination of "typical" raw waste loads for each subcategory, arithmetic average and extreme values for each parameter shown do not always include the entire range of the data collected. Some very extreme points (both low and high) were noted but rejected for use based on the premise that such data was so atypical that representative averages could not be obtained. The general rule used was that values in excess of 300 percent of the mean or less than 10 percent of the mean were rejected. One probable cause for such inconsistant raw data was poor sampling technique, (i.e., poor sampler location and/or technique, grab samples, "settling" of samples before analyzing, delays in analysis, etc.) and another cause could be inconsistant analytical work, especially between laboratories. No more than two data points for a given parameter and subcategory were rejected in the data analysis on this industry. The "number of tanneries" shown for each parameter indicates the actual number of tanneries used in that parameter average. It should be noted that some tanneries had a large amount of data from which to construct their parameter averages, while others had only one or two points per parameter; none-the-less, all plant data used was judged to be representative of typical values for the specific tannery.

Discussion of Raw Wastes

The raw waste characteristics shown in Tables V-1 and V-2 were calculated from pollutant parameters (generally recorded in mg/l), flows, and productions as supplied by the industry, governmental sources, or MRI's own sampling and plant visits. In converting to units shown, the raw wastewater data were broken down into winter and summer periods for specific years at each tannery, and where appropriate flow or production information was not supplied for that period, it was computer assigned based on best available information and trends for that plant. Included as "raw" data are those plant effluents where only screening and/or equalization are performed as pretreatment steps.

Detailed information for individual tanneries is presented as a part of the documentation submitted as a supplement to this report; however, Figures V-1 and V-2 present the BOD_5 and Cr data by subcategory as examples of the variation in the average value of the pollutant loading for plants wtihin a subcategory. Each "dot" represents the annual average of one tannery for the parameter shown, and the "bar" in each subcategory column represents the parameter mean. Asterisk marked data points were not used in averaging because they were outside the error limits discussed earlier (i.e., 300 percent or more and 10 percent or less of the subcategory average).

Examination of the information indicates the following:

1. Most data show a wide variation in values.
2. Based on average values, some plants appear to be very high or low.

Typical variation is illustrated by the BOD_5 for Subcategory 1, where the range in values is 24.0 to 98.8 kg (lb) with an average of 59.2 kg (lb) per 1,000 kg (lb) of hides. The variance of this and other parameters is undoubtedly due 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 and practices which can exist. Table V-3 shows the variation that occurs within a single tannery during one day (it should be noted that this plant operates on two shifts a day; a "typical" tannery with one shift per day would show even more variance). Production scheduling, sampling times, sample collection practices, and the differences in reporting procedures, are other contributions of variance.

Table V-1. Raw Wastewater Characteristics, kg/1000 kg of Raw Material Hide (Same as lb/1000 lbs of Hide)

	Category 1 Cattle-Pulp-Chrome			Category 2 Cattle-Save-Chrome			Category 3 Cattle-Non-Chrome			Category 4 Thru the Blue		
	Number of Tanneries	Range	Average	Tanneries	Range	Average	Tanneries	Range	Average	Tanneries	Range	Average
Flow, cu.m/kg	27	0.004 - .069	0.038	11	0.016 - .094	0.045	14	0.007 - .032	0.033	2	0.02 - .02	0.02
(gal/1b)	27	(0.52 - 8.3)	(4.6)	11	(1.9 - 11.3)	(5.5)	14	(0.9 - 8.6)	(4.0)	2	(2.41 - 2.42)	(2.4)
BOD_5	14	24.0 - 98.8	59.2	9	19.6 - 110	60	8	24.3 - 63	42	2	48 - 204	126
TSS	15	14.7 - 368	109.3	8	50 - 273	116	8	35 - 112	57	2	108 - 221	165
O&G	11	0.4 - 38	16.6	6	0.14 - 33	15.2	6	0.02 - 40	16.4	2	18 - 55	37
Total Chrome	16	0.06 - 8.8	3.15	7	0.01 - 4.5	2.4	5	0.04 - 1.6	0.53	1	--	6.3
Sulfide	10	0.05 - 9.9	2.6	7	0.05 - 6.8	2.7	5	0.004 - 6.4	2.6	1	--	7.6
TDS	10	47 - 656	319	5	206 - 373	262	2	244 - 408	326	1	--	664
TVS	7	57 - 705	216	2	50 - 143	96	5	17 - 138	60	1	--	266
COD	10	66 - 296	170	6	50 - 219	123	4	79 - 205	144	1	--	474
TKN	9	0.9 - 22	11.7	5	0.4 - 13.3	8.1	4	8 - 50	19.4	1	--	29
Ammonia N	8	1.7 - 14	5.5	4	4.4 - 7.8	6.5	3	0.4 - 5.3	3.4	1	--	11
NO_2-NO_3	5	0.02 - 0.5	0.14	3	0.26 - 0.8	0.4	2	0.02 - 0.06	0.04	1	--	0.01
Chloride	9	6 - 201	101	3	87 - 244	161	4	8.5 - 175	97	1	80 - 278	179
Alkalinity	6	21 - 76	47	2	26 - 32	29	2	11 - 86	49	1	--	78
Phenols	2	0.1 - 1.0	0.55	2	0.1 - 0.1	0.1	2	0.2 - 0.8	0.3	1	--	0.2
pH	13	6.0 - 12.4	--	6	4.4 - 13.0	--	6	4.2 - 12.6	--	1	9.2 - 10.3	--
Temperature, °C	1		26			15.5			16			
°F	1	--	79	1	--	60	1	--	61			

	Category 5 Retan, only			Category 6 No Beamhouse (NB) Tannery			Category 7 Shearlings		
	Number of Tanneries	Range	Average	Number of Tanneries	Range	Average	Number of Tanneries	Range	Average
Flow, cu.m/kg	8	0.007 - .021	0.014	10	0.007 - .058	.027	3	0.09 - .143	0.116
(gal/lb)	8	(0.8 - 2.6)	(1.7)	10	(0.9 - 7.0)	3.3	3	(10.9 - 17.2)	(13.9)
BOD_5	3	6.1 - 14	10.2	8	7.6 - 54.6	26.2	2	46 - 104	75
TSS	3	4.2 - 18	13.1	8	2.1 - 99.0	26.0	2	52 - 171	111
O&G	3	2.8 - 9.9	6.2	5	1.3 - 13.8	7.6	2	28 - 138	83
Total Chrome	3	0.3 - 1.8	1.3	6	0.1 - 2.6	1.1	1	0.8 - 14.4	3.4
Sulfide	1	0.003 - 0.007	0.005	3	0.001 - 0.11	0.06	1	0.008 - 0.16	0.05
TDS	1	60 - 66	63	5	43 - 250	130	1	--	535
TVS	1	32 - 36	34	4	18 - 57	38	1	--	82
COD	1	43 - 54	48	3	12 - 68	42	2	176 - 722	449
TKN	1	1.9 - 3.6	2.8	1	0.8 - 3.8	1.9	1	--	7.8
Ammonia, N	1	1.6 - 2.1	1.9	2	0.4 - 0.7	0.6	1	--	3.6
NO_2-NO_3	1	0.02 - 0.03	0.02	2	0.03 - 0.15	0.1	1	0.07 - 0.16	0.11
Chloride	1	0.8 - 12.6	6.7	3	15 - 72	41	1	257 - 281	269
Alkalinity	1	--	5.8	1	2.4 - 15	7.4	1	4.9 - 11.4	8.2
Phenols	1	0.2 - 0.3	0.2	1	--	0.1	1	--	2.8
pH	3	4.8 - 7.2	--	8	3.3 - 12.2	--	2	4.2 - 12.7	--
Temperature, ^oC		22.2 - 27.7	24.4						
^oF	1	72 - 82	76						

Table V-2 . Leather Tannery Raw Waste Parameters Expressed As Average Concentration for Each Category, mg/l

	Category 1 Cattle-Pulp-Chrome		Category 2 Cattle-Save-Chrome		Category 3 Cattle-Non-Chrome		Category 4 Thru the Blue		Category 5 Retan Only		Category 6 No Beamhouse Tannery		Category 7 Shearlings	
	Number of Tanneries	Average	Number of Tanneries	Average	Number of Tanneries	Average	Number of Tanneries	Average	Number of Tanneries	Average	Number of Tanneries	Average	Number of Tanneries	Average
BOD5	14	1545	9	1308	8	1255	2	6290	3	719	8	950	2	645
TSS	15	2850	8	2529	8	1700	2	8233	3	924	8	944	2	955
O&G	11	433	6	330	6	490	2	1845	3	437	5	275	2	714
Total Chrome	16	82	7	[illegible]7	5	16	1	315	3	92	6	40	1	29
Sulfide	10	68	7	76	5	78	1	380	1	.35	3	2.2	1	.4
TDS	10	8326	5	7360	2	9747	1	33134	1	4440	5	4720	1	4600
TVS	7	5638	2	2700	5	1794	1	13273	1	2397	4	1380	1	705
COD	10	4437	6	268[illegible]	4	4300	1	23652	1	3384	3	1525	2	3860
TKN	9	305	5	177	4	580	1	1447	1	197	1	69	1	67
Ammonia N	8	144	4	140	3	100	1	549	1	134	2	22	1	31
NO2-NO3	5	3.7	3	8.7	2	1.2	1	.5	1	1.4	2	3.6	1	.95
Chloride	9	2636	3	3510	4	2900	1	8932	1	472	3	1488	1	2313
Alkalinity	6	1227	2	630	2	1465	1	3892	1	409	1	268	1	70
Phenols	2	14	2	2.2	2	9	1	10	1	14	1	3.6	1	24

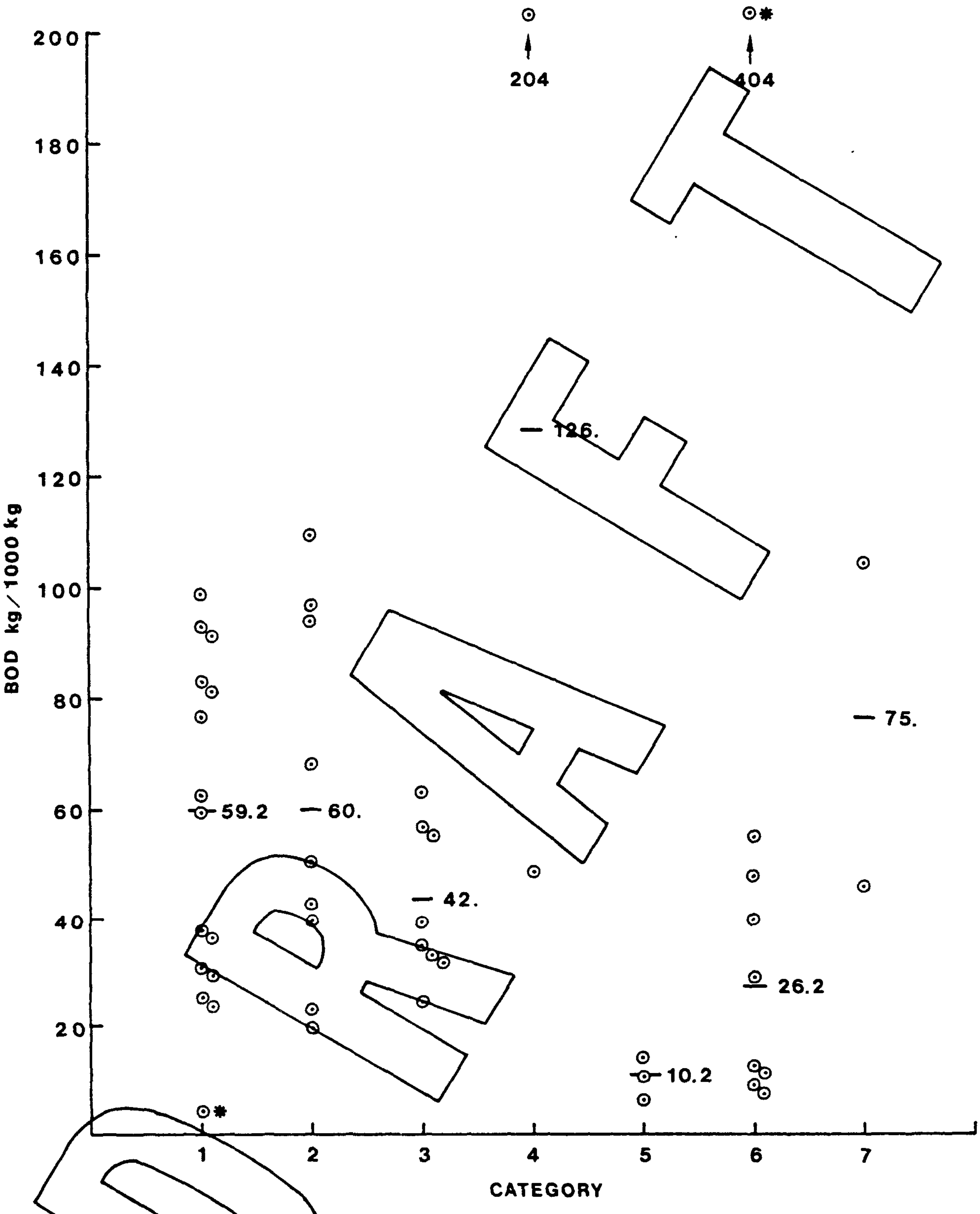


FIG. V - 1 RAW BOD DATA BY CATEGORY

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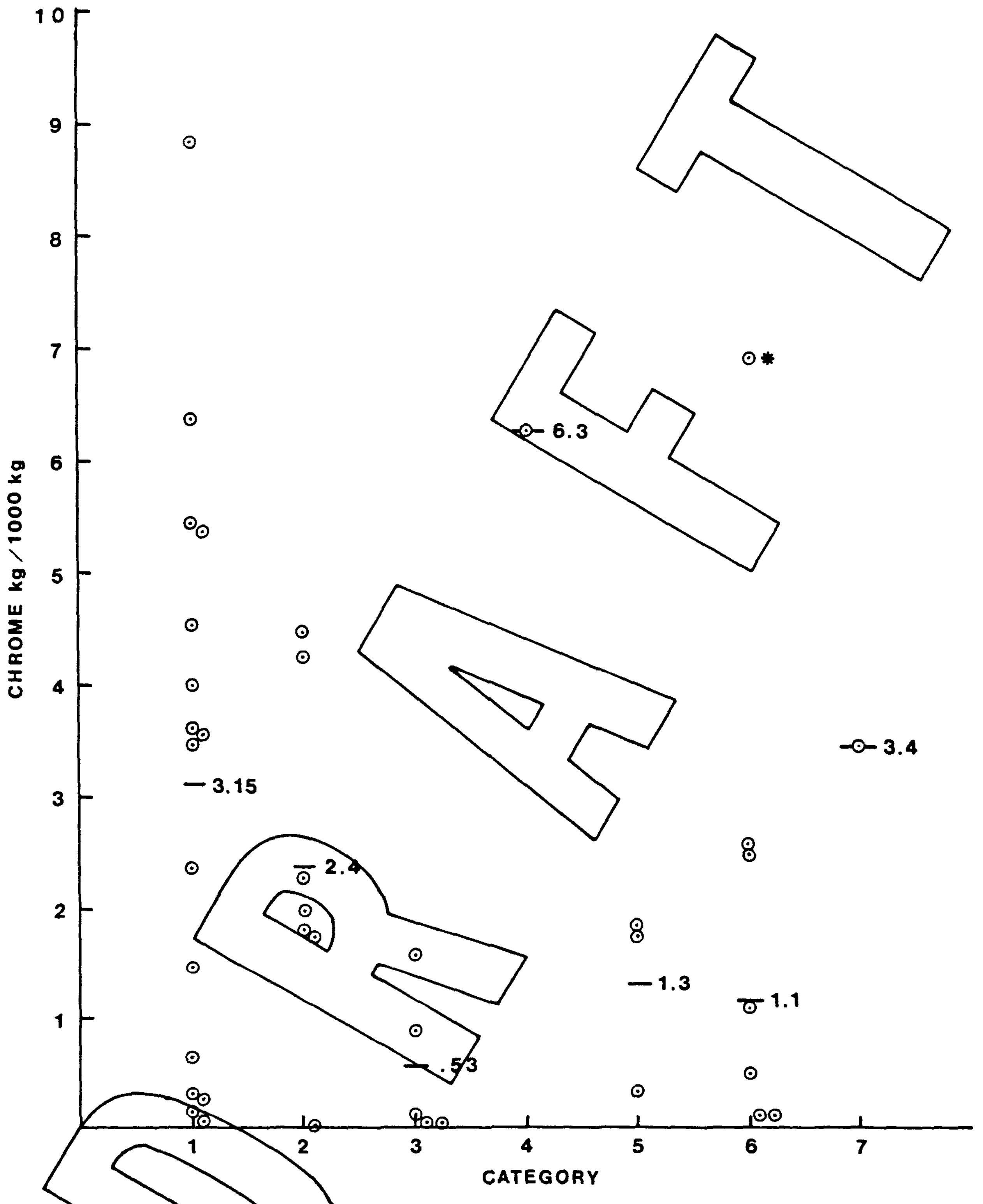


FIG. V - 2 RAW CHROME TOTAL DATA BY CATEGORY

DATA POINTS: ⊙ MEAN: —

Table V-3. Hourly Raw Waste Data for a Single Cattlehide Tannery (Category 1)

Tannery No. 237 | Data Taken 9/1-2/76

Time	Flow (mg)	BOD5 (ppm)	Suspended Solids (ppm)	Chromium Total (ppm)	TKN (ppm)	pH (S.V.)	Oil and Grease (ppm)
7 - 8 a.m.	.0592	6190	6300	116	1133	12.22	770
8 - 9 a.m.	.0523	1620	2260	36.8	333	9.48	170
9 - 10 a.m.	.0443	1320	1420	21.0	196	8.80	280
10 - 11 a.m.	.0581	1650	2080	20.2	324	9.50	160
11 - 12 noon	.0506	1370	2120	24.8	227	11.60	320
12 - 1 p.m.	.0460	1550	1920	14.5	249	11.81	230
1 - 2 p.m.	.0505	1080	760	17.2	222	9.44	270
2 - 3 p.m.	.0526	1660	1740	13.0	204	10.36	350
3 - 4 p.m.	.0347	1030	260	16.5	151	7.09	130
4 - 5 p.m.	.0337	644	180	76.5	49	7.25	160
5 - 6 p.m.	.0347	748	620	26.5	67	6.57	230
6 - 7 p.m.	.0250	862	240	81.0	58	6.43	266
7 - 8 p.m.	.0303	662	60	34.1	37	6.89	58
8 - 9 p.m.	.0201	954	1580	76.2	125	11.83	214
9 - 10 p.m.	.0241	1420	1220	236	141	6.16	1200
10 - 11 p.m.	.0221	430	240	81.5	30	6.83	192
11 - 12 Midnight	.0224	439	480	122	60	6.60	110
12 - 1 a.m.	.0243	100	60	19.3	20	7.70	34
1 - 2 a.m.	.0230	4140	7020	65.5	787	12.52	1900
2 - 3 a.m.	.0248	2210	2720	201	232	9.56	1100
3 - 4 a.m.	.0352	1690	1460	17.3	187	10.90	326
4 - 5 a.m.	.0439	2370	4400	53.2	520	12.30	635
5 - 6 a.m.	.0448	2600	6040	51.5	1378	12.34	1380
6 - 7 a.m.	.0648	3950	3820	113	920	11.95	1200

Wastewater flow data are presented in Figure V-3. As with raw waste data, significant differences within each subcategory occur due primarily to in-plant process variations and water conservation practices. The data are insufficient to determine the contribution or significance of the various factors and industry opinion is equally diverse on variability influences.

Several methods of determining the BOD5 averages or means within each subcategory were considered, including a production weighted mean. The differences in the results with different methodologies were small, however, and a simple arithmetic mean with exclusion of exceptional data points as described earlier, was calculated for the various parameters. Statistical significance tests were applied to the data where appropriate, but the results provided no further insights or understanding of wastewater parameter relationships beyond what is evident in the figures and tables contained in this section.

One of the concerns with previous analysis of the leather tanning industry was the potential variation between winter and summer values of the pollutant parameters. In order to explore this possibility, all data utilized were specifically dated as to collection time and separate analyses were performed for each season (summer was assumed to be May through October; winter, November through April). Seasonal variation in production and plant capacity expansion or reduction was accounted for in the data analysis, and only data for existing operations and processes (as of November 1, 1976) were used (however, data from two recently closed tanneries were not included). Table V-4 shows the result of the seasonal analysis by subcategory for selected parameters. As can be seen, data variation is generally not significant, and where there is variation, summer operations more often generate greater raw waste loads (much of this variation is accounted for by more summer period data availability and quality). Since significant seasonal differences were not found, the data utilized in this study reflect annual averages.

An examination of average values for the various parameters reveals that the data generally confirm what would be expected, given the tannery process variations. Some observations are worth noting. Wastewater flows are higher in the hair save operation than the pulping operation, but the BOD5 are approximately equal. Nonchrome tanning methods appear to generate less BOD5 than chrome methods. Significant amounts of chrome appear in the "retan only" tannery effluents, more in fact than in those plants that tan and retan ("No Beamhouse," Subcategory 6). In many of these cases, sample

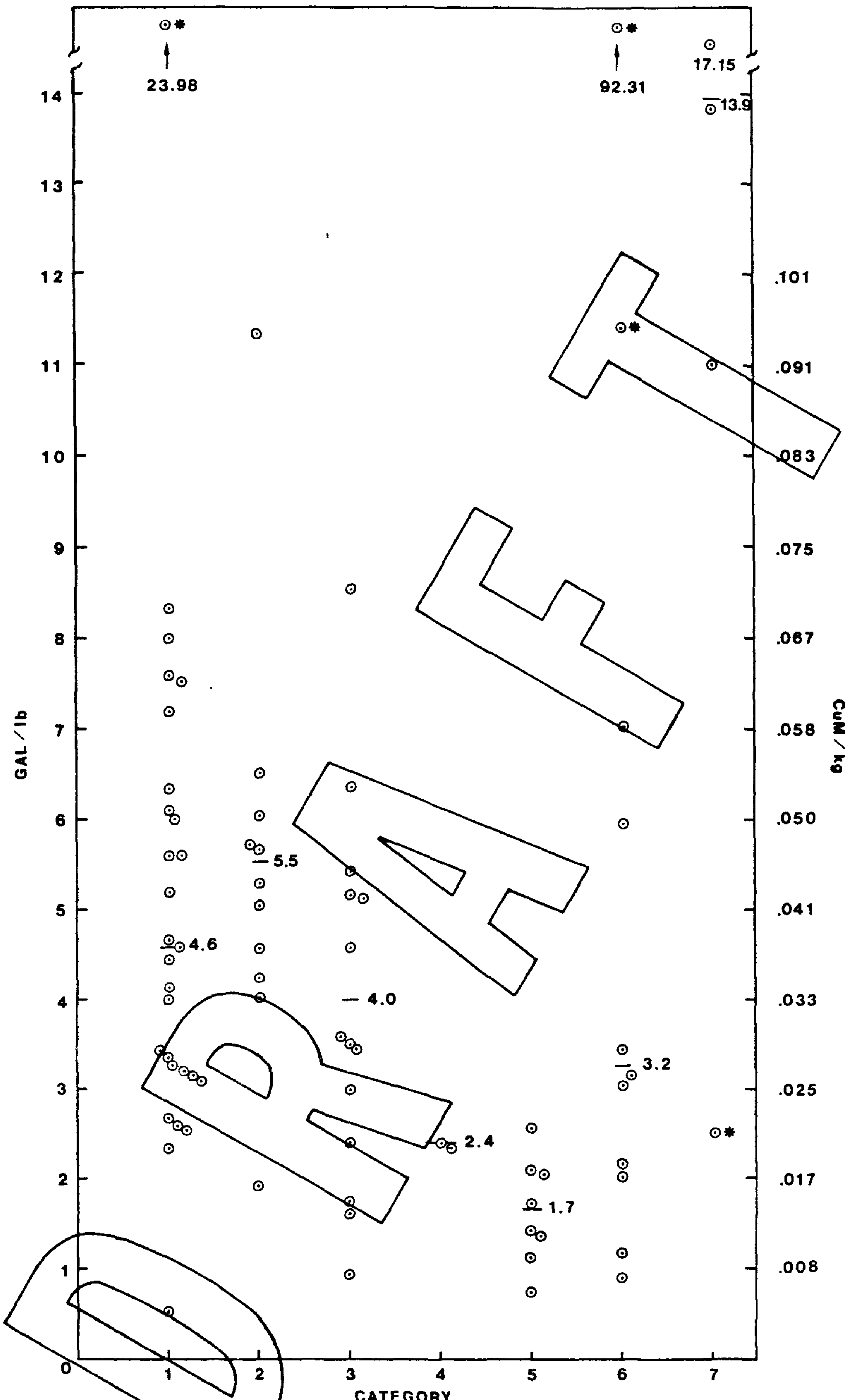


FIG. V - 3 WASTEWATER FLOW DATA BY CATEGORY

DATA POINTS: ⊙ MEAN: —

Table V-4. COMPARISON OF WINTER/SUMMER RAW WASTE CHARACTERISTICS

CATEGORY	FLOW		POLLUTANT PARAMETERS, kg/1000 kg (Same as LB/1000 LB) WINTER AVE./SUMMER AVE.				
	cu. m/Kg	gal/lb	BOD_5	TSS	O&G	TOT. CR.	SULFIDE
1	0.037/0.037	4.497/4.401	63.0/56.7	137.5/102.8	28.20/269.04	2.88/3.71	1.891/2.863
2	0.045/0.060	5.437/7.145	56.8/47.4	127.2/94.2	11.97/22.95	1.82/2.41	2.756/2.428
3	0.018/0.030	2.170/3.654	36.7/44.6	64.8/60.1	0.02/19.73	0.87/0.44	1.128/2.996
4	0.016/0.020	2.000/2.450	21.9/57.4	71.9/120	8.28/71.1	---/6.27	---/7.600
5	0.015/0.012	1.787/1.450	8.4/11.7	12.3/9.8	6.56/4.04	1.45/0.90	---/0.005
6	0.029/0.026	3.505/3.093	135.1/65.3	284.7/341.1	65.90/183.89	3.38/1.66	---/0.030
7	0.093/0.105	11.215/12.695	99.9/58.4	141.0/91.3	81.14/30.64	0.72/4.03	---/0.049

size is a significant factor in explaining these differences. Subcategory 4, "Thru-the-Blue," in principle should have parameter values equalling the difference between Subcategories 1 and 5. This relationship is not substantiated by the data; however, the small sample size (two) and the fact that one plant was exceptional preclude drawing any conclusions.

The raw waste characteristics are presented in Table V-1 for each of the seven subcategories. As described in Section IV, the rationale for subcategorization was based in part on raw waste characteristics and on tannery subprocesses in use by typical plants in each subcategory. The raw waste characteristics for a tannery, of course, are dependent on the combination of subprocesses in use in the tannery. Comparative wastewater volume and pollutant loadings originating from the tannery subcategories are given in Table V-2, and are described below.

SOURCES OF WASTEWATER AND WASTE LOAD

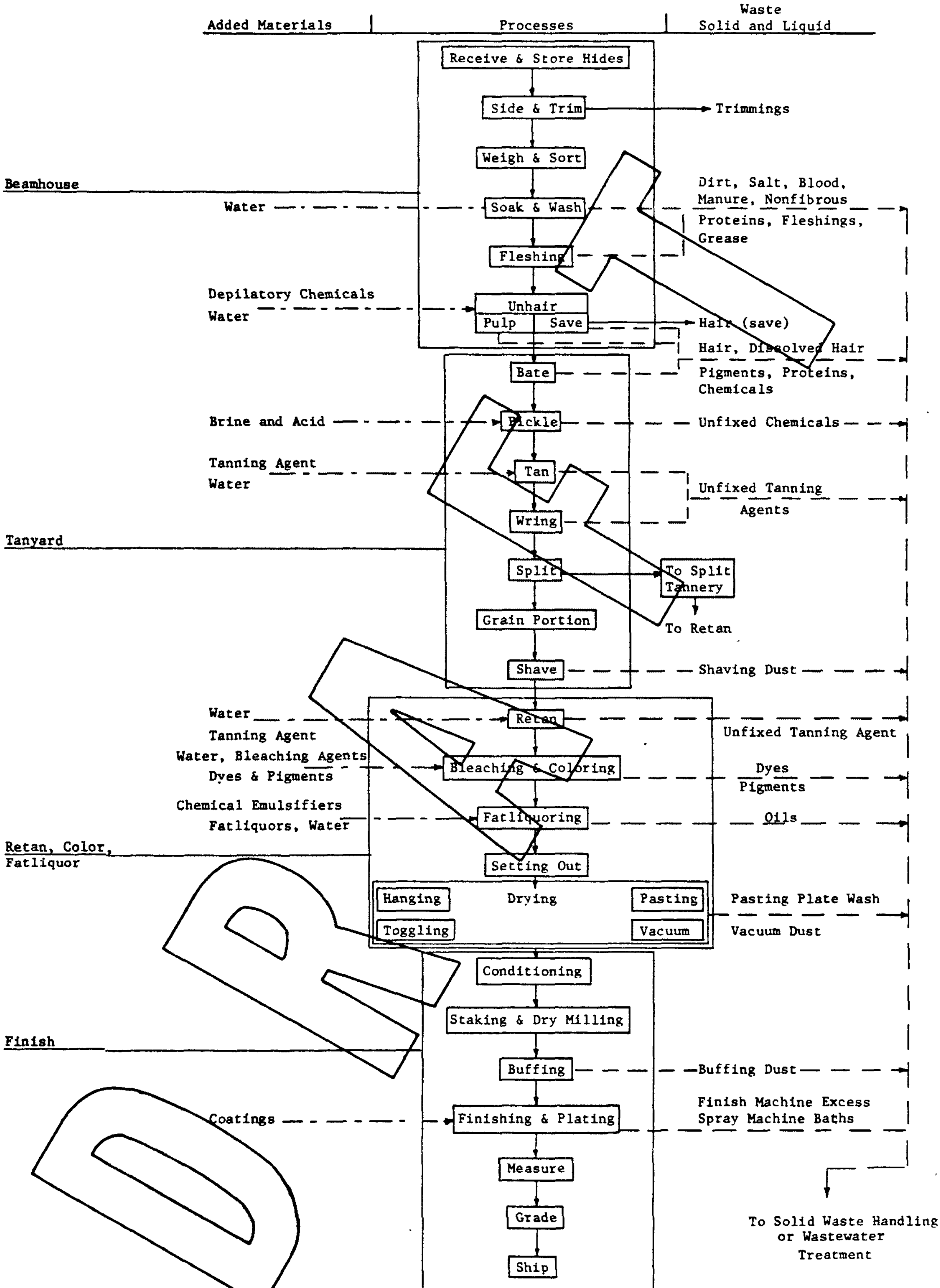
Tannery Processes

Processes which occur in various combinations in the tanning industry subcategories 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 sequence of the subprocesses and the materials used in each are presented in Figure V-4. The subprocesses are groups into the four major tanning steps--beamhouse, tanyard, and wet and dry finishing. General descriptive terms are used to identify the input materials to the processes, such as depilatory chemicals for unhairing and tanning agents for the tanning process. This figure also indicates the major solid and liquid waste streams originating from each process and the primary physical contaminants in each. Recycling and reuse of several of these waste streams is a continuing and growing trend in the industry. Such streams as the spent chrome and vegetable tanning, unhairing lime-sulfide, and the pickling solution are those most frequently considered for reuse, recycle, or materials recovery. The chrome tanning solution is most often managed for reuse, followed by the pickling solution, among the U.S. tanners. It is reported that European tanneries are being advised to give

Figure V-4
PRODUCT AND WASTEWATER FLOW FOR GENERALIZED
LEATHER TANNING AND FINISHING PLANTS



serious consideration to protein precipitation and recovery as a by-product from the beamhouse waste stream to reduce the waste load and to produce a by-product of value[3].

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 materials 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 hide. The wastewater volume from this process is estimated from industry data to average about 20 percent and to vary from 10 to 35 percent of the total wastewater flow.

Primary waste constituents from this process are BOD5, COD, suspended solids, and dissolved 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)
BOD5	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 as a solid waste 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--Degreasing operations are not normally performed on cattlehide, but more commonly on sheepskins and pigskins. Two types of degreasing are used:

1. Hot water with detergent.
2. Solvent.

In both cases the grease is separated and recovered as a by-product of value. However, some grease is not captured and enters the plant waste stream. In the case of solvent degreasing, the solvent is also recovered. In addition to grease, BOD5, COD, and suspended solids are other waste constituents of the waste stream from this process.

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[1]. The quantity entering the waste stream is minimized and usually is only a small part of the total. Reliable data on the grease content of the waste stream from the degreasing operation are not available. A major problem arises from the difficulty in obtaining a truly representative sample of such a stream.

Unhairing--Two processes are used for unhairing:

1. Hair save.
2. Hair pulp (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 dissolved solids. A part of the soluble solids is the sodium chloride not removed in the soak and wash operation.

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 if it is to be baled and sold as a product. Washing is unnecessary if the hair is only going to be disposed of as a solid waste. The waste water from washing contains the same waste constituents as the unhairing solution, only in a more dilute 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 unhairing solution. The wastewater, therefore, has a higher content of waste constituents, particularly sulfides and nitrogen.

A few tanneries currently use an intermediate hair removal process between the two extremes of pulp or save. This semi-pulp unhairing process is a natural outgrowth of a more traditional hair save operation where by-product hair markets no longer exist or the cost of hair washing, baling, and selling exceeds income for the hair. Moreover rather than making a complete shift to a hair pulp beamhouse, some tanners have merely made marginal increases in concentrations of unhairing chemicals and retain the use of unhairing machines. Also a desire to retain the hair save option and a lack of experience with hair pulping prevent rapid change from an essentially hair save to a hair pulp beamhouse. In semi-pulp the hair is solubilized less than in hair pulp but more than in hair save. The individual hairs do retain their integrity but this is of lesser concern because the hair is not to be used as a by-product. Wastewater flow rate and waste loading for the semi-pulp process would intuitively fall between the two extremes, although no data are available to confirm this.

The unhairing subprocess as reported by tanneries in this study sample generates between 20 and 38 percent of the total wastewater flow from a cattlehide tannery. The average is 32 percent of the total wastewater flow among those reporting such information.

For a cattlehide chrome tannery, BOD5 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[1].

Bating--The bating process is used to delime, reduce swelling, peptize the fibers, and remove protein degradation products. Major chemical additions are ammonium sulfate to reduce pH to the appropriate 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[1].

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 primarily contain sulfuric acid and salt, although a small amount of a wetting agent and biocide are sometimes used. Protein degradation products, lime, and other waste constituents have been previously removed, thus the quantities of BOD5, suspended solids, and nitrogen are low. Principal waste constituents are the acid and salt. The strong liquor dump frequently made after the tanning process is a source of significant waste because of the accumulation of waste materials from these several processes. Bate and pickle waste water volumes were reported as a combined total by several tanneries. The proportion of total wastewater flow from the bate and pickle processes as reported is from 9 percent to 50 percent with an average and median of 26 percent of total tannery wastewater.

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, zirconium, and other metal salts, and gluteraldehyde and formaldehyde can also be used.

In the chrome process, a basic chromic sulfate or a 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 tannage 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 entry of hexavalent chromium into the waste system is by spillage.

The spent chromium tanning solution is relatively low in BOD5 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 strengths. Because of the cost of tanning materials, process solution conservation has been practiced. Therefore, that part of the solution entering the waste stream is due to drag-out or planned blowdown to maintain tanning solution quality. Vegetable tannin in the waste is a source of both BOD5 and color.

The reported wastewater volume from tanning varies from about 1 percent to 26 percent of total tannery waste. The latter figure is unusually high because it represents a tannery processing only through the blue stage. The median percent is 4.4 and the average is 6.6 among the tanneries reporting this data.

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 wastewater is not strong; usually this process does not add a significant quantity to the total waste flow.

The most variable 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 but instead are 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 in types and amount of oil added in this process, depending upon the end use of the leather. The use of mineral oils in this process is very small however it does occur. Such oils are not as amenable to biological treatment as those presently in widespread use.

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 degrees C (100 degrees F)[1]. 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 wastewater, recycling is not normally practiced. Use of high temperatures in retanning will enable maximum uptake of chromium and reduce the discharge of this constituent.

The wastewater volume reported from these processes as a percent of total tannery waste is highly variable, ranging from 12 to 30 percent. An average figure would be misleading because of the few tanneries reporting such information.

<u>Finishing</u>--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, very little blowdown flows into the waste stream. This pasting water is prepared by mixing water and starch; thus, it is quite high in concentration even though the volume is very low. Most leather finishes do not have a contaminated wastewater discharge from their processing activities.

TOTAL PLANT LIQUID WASTE

The quantity of wastewater is important to the economics of treatment because a number of the unit operations performed in waste 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 afford major reductions in waste constituents from the total plant waste stream.

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

WASTEWATER PARAMETERS OF SIGNIFICANCE

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

- Biochemical Oxygen Demand (5-day, 20 degrees C., BOD_5)
- Total Chromium
- Oil and Grease
- Sulfide
- Total Suspended Solids (TSS)
- Nitrogen Content (Ammonia Nitrogen and Total Kjeldahl Nitrogen)
- pH and Alkalinity

Wastewater parameters of minor significance are:

- Total Dissolved Solids
- Chlorides
- Chemical Oxygen Demand
- Total Volatile Solids
- Nitrates and Nitrites
- Phenols
- Fecal Coliforms

RATIONALE FOR THE SELECTION OF MAJOR POLLUTANT PARAMETERS

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand is the quantity of oxygen required for the biological and chemical oxidation of waterborn substances under ambient or test conditions. Materials which may contribute to the BOD include: carbonaceous organic materials usable as a food source by aerobic organisms; oxidizable nitrogen derived from nitrites, ammonia and organic nitrogen compounds which serve as food for specific bacteria; and certain chemically oxidable materials such as ferrous iron, sulfides, sulfite, etc., which will react with dissolved oxygen or are metabolized by bacteria. In most leather tannery wastewaters, the BOD derives principally from organic materials and from ammonia (which is itself derived from animal or vegetable matter).

The BOD of a waste exerts an adverse effect upon the dissolved oxygen resources of a body of water by reducing the oxygen available to fish, plant life, and other aquatic species. Conditions can be reached where all of the dissolved oxygen in the water is utilized resulting in anaerobic conditions and the production of undesirable gases such as hydrogen sulfide and methane. The reduction of dissolved oxygen can be detrimental to fish populations, fish growth rate, and organisms used as fish food. A total lack of oxygen due to the exertion of an excessive BOD can result in the death of all aerobic aquatic inhabitants in the affected area.

Water with a high BOD indicates the presence of decomposing organic matter and associated increased bacterial concentrations that degrade its quality and potential uses. A by-product of high BOD concentrations can be increased algal concentrations and blooms which result from decomposition of the organic matter and which form the basis of algal populations.

The BOD5 (5-day BOD) test is used widely to estimate the pollutional strength of domestic and industrial wastes in terms of the oxygen that they will require if discharged into receiving streams. The test is an important one in water pollution control activities. It is used for pollution control regulatory activities, to evaluate the design and efficiencies of wastewater treatment works, and to indicate the state of purification or pollution of receiving bodies of water.

Complete biochemical oxidation of a given waste may require a period of incubation too long for practical analytical test purposes. For this reason, the 5-day period has been accepted as standard, and the test results have been designated as BOD5. Specific chemical test methods are not readily available for measuring the quantity of many degradable substances and their reaction products. Reliance in such cases is placed on the collective parameter, BOD5, which measures the weight of dissolved oxygen utilized by microorganisms as they oxidize or transform the gross mixture of chemical compounds in the wastewater. The biochemical reactions involved in the oxidation of carbon compounds are related to the period of incubation. The five-day BOD normally measures only 60 to 80 percent of the carbonaceous biochemical oxygen demand of the sample, and for many purposes this is a reasonable parameter. Additionally, it can be used to estimate the gross quantity of oxidizable organic matter.

The BOD5 test is essentially a bioassay procedure which provides an estimate of the oxygen consumed by microorganisms utilizing the degradable matter present in a waste under conditions that are representative of those that are likely to occur in nature. Standard conditions of time, temperature, suggested microbial seed, and dilution water for the wastes have been defined and are incorporated in the standard analytical procedures. Through the use of this procedure, the oxygen demand of diverse wastes can be compared and evaluated for pollution potential and to some extent for treatability by biological treatment processes.

Because the BOD test is a bioassay procedure, it is important that the environmental conditions of the test be suitable for the microorganisms to function in an uninhibited manner at all times. This means that toxic substances must be absent and that the necessary nutrients, such as nitrogen, phosphorus, and trace elements, must be present.

Total Chromium (CrT)

Chromium compounds are used extensively throughout the leather tanning industry. The compounds used are nearly all in the trivalent form; use of hexavalent chrome is nearly obsolete. The prevalent chromium form found in the wastewaters is trivalent chromium, although hexavalent compounds may also occur in waste streams primarily from spillage. However, the distribution cannot be determined accurately. Current analytical procedures for hexavalent chromium are such that differentiation between the valent states in a wastewater sample collected in a tannery and then transported to an analytical laboratory is essentially precluded, even though such differentiation is desirable for this industry.

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date. The recommendation for public water supplies is that such supplies contain no more than 0.05 mg/l total chromium.

The toxicity of chromium salts to fish and other aquatic life varies widely with the species, temperature, pH, valence of the chromium and synergistic or antagonistic effects, especially that of hard water. Studies have shown that trivalent chromium is more toxic to fish of some types than hexavalent chromium. Other studies have shown opposite effects. Fish food organisms and other lower forms of aquatic life are extremely sensitive to chromium and it also inhibits the growth of algae. Therefore, both hexavalent and trivalent chromium must be considered harmful to particular fish or organisms.

Oil and Grease

Because of nature of the material processed, oil and grease occur often in the leather tanning wastewater streams. The oil and grease in tannery wastewater originate as a result of the degreasing process used in some tanneries and from the oils used directly in the leather processing, especially fatliquoring. Most of these oil and grease materials are animal or vegetable based and therefore amenable to removal through biological treatment. A very small amount of mineral based oil is being used by some tanneries. This material also enters the waste stream, although presumably in very small quantities. It is a more refractory material and therefore must be removed primarily by physical-chemical waste treatment processes. These compounds can settle or float and may exist as solids or liquids. Oils and grease even in small quantities cause troublesome taste and odor problems. Scum lines from these agents are produced on water treatment basin walls and other containers. Fish and water fowl are adversely affected by oils in their habitat. Oil emulsions may adhere to the gills of fish causing suffocation, and the flesh of fish is tainted when microorganisms that were exposed to waste oil are eaten. Deposition of oil in the bottom sediments of water can serve to inhibit normal benthic growth. Oil and grease exhibit an oxygen demand.

Levels of oil and grease which are toxic to aquatic organisms vary greatly, depending on the type and the species susceptibility. It has been recommended that public water supply sources be essentially free from oil and grease.

Oil and grease in quantities of 100 l/sq km (10 gallons/sq mile) show up as a sheen on the surface of a body of water. The presence of oil slicks prevent the full aesthetic enjoyment of water. The presence of oil in water can also increase the toxicity of other substances being discharged into the receiving bodies of water. Municipalities frequently limit the quantity of oil and grease that can be discharged to their wastewater treatment systems by industry.

Sulfide

A significant portion of alkaline sulfides contained in tannery wastewater 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 and corrosion of equipment in POTW's. 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 effluent.

Sulfide does not pass through biological treatment systems because it is oxidized to sulfates which are innocuous in their normal concentrations.

Total Suspended Solids (TSS)

Suspended solids include both organic and inorganic materials. The inorganic compounds include sand, silt, and clay. The organic fraction includes such materials as grease, oil, and animal and vegetable waste products. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed; they are often damaging to the life in water. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a food source for sludgeworms and associated organisms.

Disregarding any toxic effect attributable to substances leached out by water, suspended solids may kill fish and shellfish by causing abrasive injuries and by clogging the gills and respiratory passages of various aquatic life because they screen out light, and they promote and maintain the development of noxious conditions through oxygen depletion. This results in the killing of fish and fish food organisms. Suspended solids also reduce the recreational value of the water.

Nitrogen Content (Ammonia Nitrogen and Total Kjeldhal Nitrogen

Ammonia (NH_3). Ammonia occurs in surface and ground waters as a result of the decomposition of nitrogenous organic matter. It is one of the constituents of the complex nitrogen cycle. Because ammonia may be indicative of pollution and because it increases the chlorine demand, it is recommended that ammonia nitrogen in public water supply sources not exceed 0.5 mg/l.

Ammonia exists in its non-ionized form only at higher pH levels and is most toxic in this state. The lower the pH, the more ionized ammonia is formed, and its toxicity decreases. Ammonia can exist in several chemical combinations including ammonium chloride and other salts.

Evidence exists that ammonia exerts a toxic effect on all aquatic life depending upon the pH, dissolved oxygen level, and the total ammonia concentration in the water. A significant oxygen demand can result from the microbial oxidation of ammonia. Approximately 4.5 grams of oxygen are required for every gram of ammonia that is oxidized. Ammonia can add to eutrophication problems by supplying nitrogen to aquatic life.

Total Kjeldahl Nitrogen (TKN). Total Kjeldahl nitrogen is ammonia nitrogen plus organic nitrogen content in wastewater. 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 wastewater.

pH and Alkalinity

pH. Although not a specific pollutant, pH is related to the acidity or alkalinity of a wastewater stream. It is not a linear or direct measure of either, however, it may properly be used as a surrogate to control both excess acidity and excess alkalinity in water. The term pH is used to describe the hydrogen ion--hydroxyl ion balance in water. Technically, pH is the hydrogen ion concentration or activity present in a given solution. pH numbers are the negative logarithm of the hydrogen ion concentration. A pH of 7 generally indicates neutrality or a balance between free hydrogen and free hydroxyl ions. Solutions with a pH above 7 indicate that the solution is alkaline, while a pH below 7 indicates that the solution is acid.

Knowledge of the pH of water or wastewater is useful in determining necessary measures for corrosion control, pollution control, and disinfection. To protect POTW's from corrosion, pH levels of wastewaters entering the sewerage system must be kept above 5. Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and such corrosion can add constituents to drinking water such as iron, copper, zinc, cadmium, and lead. Low pH waters not only tend to dissolve metals from structures and fixtures but also tend to redissolve or leach metals from sludges and bottom sediments. The hydrogen ion concentration can affect the "taste" of the water and at a low pH, water tastes "sour."

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity* to aquatic life of many materials is increased by changes in the water pH. For example, metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. Similarly, the toxicity of ammonia is a function of pH. The bactericidal effect of chlorine in most cases is less as the pH increases, and it is economically advantageous to keep the pH close to 7.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Alkalinity. Alkalinity is defined as the ability of a water to neutralize hydrogen ions. It is usually expressed as the calcium carbonate equivalent of the hydrogen ions neutralized.

Alkalinity is commonly caused by the presence of carbonates, bicarbonates, hydroxides, and to a lesser extent by borates, silicates, phosphates and organic substances. Because of the nature of the chemicals causing alkalinity, and the buffering capacity of carbon dioxide in water, very high pH values are seldom found in natural waters.

Excess alkalinity as exhibited in a high pH value may make water corrosive to certain metals, detrimental to most natural organic materials and toxic to living organisms.

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*The term toxic or toxicity is used herein in the normal scientific sense of the word, not the legal.

RATIONALE FOR THE SELECTION OF MINOR POLLUTANT PARAMETERS

Total Dissolved Solids (TDS)

Tannery wastes are high in dissolved solids. The largest portions 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.

Chlorides (Cl)

The preponderant fraction of tannery dissolved solids is chlorides. Used in conjunction with total dissolved solids, this parameter indicates percentages of other dissolved solids. Chloride content is important for water reuse considerations.

Chemical Oxygen Demand (COD)

Chemical oxygen demand is a purely chemical oxidation test devised as an alternate method of estimating the total oxygen demand of a wastewater. Since the method relies on the oxidation-reduction system of chemical analyses rather than on biological factors, it is more precise, accurate, and rapid than the BOD test. The COD test is widely used to estimate the total oxygen demand (ultimate rather than 5-day BOD) to oxidize the compounds in a wastewater. It is based on the fact that organic compounds, with a few exceptions, can be oxidized by strong chemical oxidizing agents under acid conditions with the assistance of certain inorganic catalysts.

The COD test measures the oxygen demand of compounds that are biologically degradable and of many that are not. Pollutants which are measured by the BOD5 test will be measured by the COD test. In addition, pollutants which are more resistant to biological oxidation will also be measured as COD. COD is a more inclusive measure of oxygen demand than is BOD5 and will result in higher oxygen demand values than will the BOD5 test.

The compounds which are more resistant to biological oxidation are becoming of greater and greater concern, not only because of their slow but continuing oxygen demand on the resources of the receiving water, but also because of their potential health effects on aquatic life and humans. Many of these compounds result from industrial discharges and some have been found to have carcinogenic, mutagenic, and similar adverse effects, either singly or in combination. Concern about these compounds has increased as a result of demonstrations that their long life in receiving waters--the result of a slow biochemical oxidation rate--allows them to contaminate downstream water intakes. The commonly used systems of water purification are not effective in removing these types of materials and disinfection such as chlorination may convert them into even more hazardous materials.

Total Volatile Solids (TVS)

Total volatile solids is an approximate measure of the organic fraction of wastewater. It is primarily useful in analyzing the treatability of the waste with biological treatment methods. A high percentage of volatile solids to total solids in the waste indicates that conventional treatment processes may, with proper design, be effective in pollution control.

Nitrates (NO_3) and Nitrites (NO_2)

Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria.

Nitrates are considered to be among the objectionable components of mineralized waters. Excess nitrates cause irritation to the gastrointestinal tract, causing diarrhea and diuresis. Methemoglobinemia, a condition characterized by dyanosis and which can result in infant and animal deaths, can be caused by high nitrate concentrations in waters used for feeding. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit.

Phenols

Phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in tannery wastewater (usually from biocide application during the leather making process). Chlorination of such waters can produce odoriferous and objectionable tasting chlorophenols which may include o-chlorophenol, p-chlorophenol, 2,6-dichlorophenol, and 2,4-dichlorophenol.

Although described in the technical literature simply as phenols, the phenol waste category can include a wide range of similar chemical compounds. In terms of pollution control, reported concentrations of phenols are the result of a standard methodology which measures a general group of similar compounds rather than being based upon specific identification of the single compound, phenol (hydroxy-benzene).

Phenolic compounds may adversely affect fish in two ways: first, by a direct toxic action, and second, by imparting a taste to the fish flesh. The toxicity of phenol towards fish increases as the dissolved oxygen level is diminished, as the temperature is raised, and as the hardness is lessened. Phenol appears to act as a nerve poison causing too much blood to get to the gills and to the heart cavity and is reported to have a toxic threshold of 0.1-15 mg/l.

Mixed phenolic substances appear to be especially troublesome in imparting taste to fish flesh. Chlorophenol produces a bad taste in fish far below lethal or toxic doses. Threshold concentrations for taste or odor in chlorinated water supplies have been reported as low as 0.00001-0.001 mg/l. Phenols in concentrations of only one part per billion have been knonw to affect water supplies.

The ingestion of concentrated solution of phenol by humans results in severe pain, renal irritation, shock, and possibly death. A total dose of 1.5 grams may be fatal. Phenols can be metabolized and oxidized in waste treatment facilities containing organisms acclimated to the phenol concentration in the wastes.

<u>Fecal Coliforms</u>

Fecal coliforms are used as an indicator since they have originated from the intestinal tract of warm blooded animals. Their presence in water indicates the potential presence of pathogenic bacteria and viruses.

The presence of coliforms, more specifically fecal coliforms, in water is indicative of fecal pollution. In general, the presence of fecal coliform organisms indicates recent and possibly dangerous fecal contamination. When the fecal coliform count exceeds 2,000 per 100 ml there is a high correlation with increased numbers of both pathogenic viruses and bacteria.

Many microorganisms, pathogenic to humans and animals, may be carried in surface water, particularly that derived from effluent sources which find their way into surface water from municipal and industrial wastes. The diseases associated with bacteria include bacillary and amoebic dysentery, Salmonella gastroenteritis, typhoid and paratyphoid fevers, leptospirosis, chlorea, vibriosis and infectious hepatitis.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

GENERAL

This section describes waste treatment technology currently available to achieve effluent limitation guidelines for the leather tanning and finishing industry. Three approaches are presented effecting various degrees of pollutant reduction. These approaches are: (1) in-process methods of reducing waste (2) preliminary treatment, and (3) secondary treatment.

Preliminary treatment (pretreatment) is defined as wastewater treatment on the plant site before discharge to a municipal treatment system. Pretreatment consists of physical-chemical treatment and intermediate storage before discharge into a secondary (biological) treatment system. It is necessary to reduce shock loads, protect the biological system, remove the suspended solids that resist treatment, prevent damage to sewer lines, and reduce health hazards in sewerage maintenance. Although it is defined as preliminary to treatment in municipal plants, pretreatment is equally applicable to an on-site or other company-owned secondary treatment system.

Secondary treatment is typically a biological process to remove organic material. A major reduction of BOD_5 and suspended solids is accomplished in secondary treatment, as well as some degree of nitrification, depending on the system. Secondary treatment technologies will not be described in this report. The second development document which is to be issued for BPT effluent limitations, as indicated in Section III, will describe these technologies.

CURRENT PRACTICES

Current practices in the tanning industry range from no treatment of wastewater to secondary treatment. In general, effluent quality requirements for tanneries discharging to municipal sewer systems are less stringent than for plants that discharge directly to surface waters. This is reflected in the survey made of 91 wet-process tanners that indicates 12 percent of the tanners discharging to municipal systems have no pretreatment, whereas all direct dischargers surveyed have at least preliminary treatment. Further, 100 percent of the direct dischargers are operating some type of secondary treatment or equivalent. With increasing numbers of municipalities imposing more stringent effluent limitations, there is a trend toward some pretreatment by all tanners.

The infromation collection forms and questionnaires, site visits, and verification sampling visits of wet processors yielded the following breakdown of current control practices in the tanning industry:

Discharge to municipal treatment plants--
90 percent of tanners:

	Percent of Dischargers (%)
Preliminary treatment	88
Coarse screening only	20
No preliminary treatment	12
Secondary treatment	0

Discharge to surface water--
10 percent of tanners

No preliminary treatment	0
Preliminary treatment only	23
Secondary treatment	77
Lagoon treatment	63
Activated sludge treatment	14

The wastewater characteristics vary among tanneries due to several factors, as described in Sections IV and V, type and condition of raw hide, final product, processes and process equipment used (e.g., hide processors), tanning agent, etc. Basically the pollutants differ little from those in wastewaters of many other industries and can be treated by conventional methods--suspended solids reduction, oil and grease removal, pH control, and BOD5 reduction. Specific constituents peculiar to certain tanning processes, such as chromium and sulfide, can be removed with available treatment methods currently practiced by the industry.

The interrelationship of the different media for pollutant discharge, i.e. air, water, and solid waste, cannot be overlooked when tannery waste is treated. As an example, plain sedimentation and sludge dewatering produce a waste product for land disposal. If a chrome tan process is being used, this waste may contain chromium and care must be exercised in managing the waste disposal to prevent leachate contamination of ground or surface waters. The practice of chrome reuse or recovery within the plant should reduce the chromium content of the sludge.

Each treatment approach in this discussion is examined with a description of equipment, examples of systems currently being used, and reduction levels expected.

RELATIONSHIP OF PRETREATMENT TECHNOLOGY TO PUBLICLY OWNED TREATMENT WORKS REQUIREMENTS

Tannery wastes can and have created the following problems for POTW's:

* large pieces of scrap hide and leather clogging or fouling operating equipment;
* excessive quantities of hair and other small scale, screenable solids;
* highly acidic or alkaline waste streams;
* wastewater flow surges;
* excessive loadings of suspended and settleable solids and BOD5, consistently or in surges;
* odors, facilities corrosion, and hazardous gas generation from sulfide bearing wastes;
* a potential future problem with disposal of sludges containing chrome.
* pass through of ammonia nitrogen

Each of these problems can be significantly reduced or eliminated by applying pretreatment technology in leather tanneries. Fine screening can be very effective in removing hair, fibers, and scrap material from wastewater. The screening equipment must be more than a simple bar screen. Fine screening is available in many different configurations, some of which are particularly effective on tannery type wastes. An example is the three-slope static screen made of specially coined curved wires using the Coanda or wall attachment phenomenon to withdraw the fluid from the under layer of a slurry which is stratified by controlled velocity over the screen. This method has been found to be highly effective in handling slurries containing fatty or sticky fibrous suspended matter[4] and is in use in the leather tanning industry. Screening equipment also must be installed, operated, and maintained properly to function well.

Waste streams from specific processes in tanneries can be highly acidic or alkaline. If such streams are discharged without pH adjustment or mixing with a different neutralizing stream, the waste stream may create problems within the sewer or at the treatment plant. A pH control mechanism of holding and mixing various wastes or of directly adjusting the pH of the waste is readily implemented as a pretreatment technology.

Flow and waste loading surges can be particularly disruptive to biological treatment systems such as are used in POTW's, and they can be minimized by providing equalization to smooth the rate of flow or waste loading discharge. If space limitations at a tannery preclude an equalization tank, discharge scheduling, as practiced at one tannery at least, can reduce the magnitude of these surges.

Catch basins, wet wells and other pretreatment facilities that provide a retention time and space for solids separation from the waste stream can be very effective if designed and maintained properly. Such a facility requires regular maintenance if it is to operate consistently and effectively.

If necessary, the potential problem of disposing municipal sludge that contains chrome can be shifted back to the tannery where a smaller quantity of sludge containing a higher concentration of chrome is more easily disposed of in a controlled environment. Chrome recovery and reuse technology is also available and in use by the industry. This substantially reduces the chrome content of the waste stream and of sludges generated in treatment of these wastes.

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.

A reduction in pollutants and in the costs of waste treatment often can be effected by the following steps:

1. Process changes.
2. Substitution of process ingredients.
3. Water conservation.
4. Repair and replacement of leaky or faulty equipment.
5. Installation of automatic monitoring devices to detect abnormal quantities of selected constituents in waste effluents.
6. Process solution reuse or recovery.

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

In the tanning industry, process changes have been difficult to make because of the diversity of tanning methods employed. While tanning operations traditionally have been carried out on a batch basis, it is possible that more of the chemical applications as well as the washing and rinsing could be handled more effeciently on a counter-current continuous flow basis, and thus be more efficient in chemical and water usage. In this way, maximum utilization of all active ingredients could be achieved, thereby leaving only concentrated wastes of small volumes for treatment and disposal. Substitution of effluents from one process for make-up water in another generally is feasible at some points within a tannery. Before this change can be made, however, it is necessary that the quantity of water required for each operation be established.

The substitution of chemical ingredients of low pollution potential for those which are problem pollutants often can be used to advantage in industrial processes. In tanning, for example, it is possible to use dimethylamine as a depilatory agent in the place of the sulfides which contribute heavily to the problems of waste treatment and disposal. The difficulties resulting from the high concentrations of contaminants in spent tan liquors from a vegetable tanning process using extracts from bark and other plant materials have been lessened by recovery and reuse of those spent liquors and by the use of synthetic tanning agents (syntans).

A survey of water needs in a tannery will go far toward reducing the volume of wastes because water usage is generally in excess of the quantity needed. Some methods of water conservation are listed below:

1. Encourage employees to implement any potential water saving practices. Eliminate the constantly running hoses observed in (a few) tanneries (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 float volumes.
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 makeup.

5. Use of processing equipment, such as hide processors, pumpable drums (rather than floor dumping), float storage tanks, and other reuse equipment.
6. Recirculation of non-contact cooling water, such as for vacuum driers.

Tannery No. 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 recirculation of hair wash water by installation of a fine screen for solids removal. Through the installation of a vegetable tanning 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 (modified 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 hair pulp processes. A summary explaining the utilization of the hide processor in reducing tanning effluent is given by Larsen[5].

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 No. 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)[6]. 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 No. 3 uses the same water for washing following their "modified pickle" operation and their vegetable tanning operation[6]. Tannery No. 1 uses a similar process for recycling the soak water following the vegetable tanning operation back to the color operation that precedes vegetable tanning[6]. There are also some indications that spent liquors previously used in vegetable tanning are reused in retan operations. Tannery No. 4 indicates that they are using bate wastewater for alum tanning make-up water[6]. Tannery No. 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 hair pulp process and for wash water following the bate process[6].

Industrial waste problems are often complicated or intensified by the fact that faulty or obsolete process equipment is kept in service without proper repair or replacement. Operating personnel likewise can be a liability in waste disposal because large quantities of usable materials often are lost through careless or accidental spills or through excessive drainage of liquids from hides as they are transferred from one process to another. Acquainting operators with the importance of eliminating these sources of wastes often will simplify waste disposal problems.

No waste reduction and elimination program can be complete without adequate control measures. Automatic monitoring equipment for detecting abnormal levels of selected constituents is extremely valuable as a safeguard against the failure of established precautionary measures. For example, abnormal and accidental discharges of concentrated lime or tan solutions could be detected immediately by pH meters and alarms installed on the effluent lines from these processes. In addition to indicating loss of materials, automatic sensing devices can be used to operate recovery equipment.

The most efficient method for eliminating pollutants from tannery wastes and in reducing the volume of effluent is through reuse of water and chemical agents and through recovery of materials which are normally wasted.

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[7].

There are a number of vegetable tanneries that are using recycle systems to reduce the amounts of tan liquor that are discharged into the waste streams. The Liritan process employs such a technique by counter-current flow of tannage in relation to the hides. 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[8] 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.

Tannery No. 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[6]. 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 system, however, a substantial portion was recycled and only a small amount wasted.

Tannery No. 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 conceivably be reused indefinitely. The spent liquor was drained and settled in much 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 the 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 No. 7, a shearling tannery, has been able to reuse its chrome tan solution up to five times[6]. Because of processing requirements, spent chrome tan liquors are not at present being reused.

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

Tannery No. 8 reports reusing retan liquors[6]. Tannery No. 9 reports reusing the finishing oils[6]. 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 processes, chrome tanneries should consider installing reuse, recycle, or recovery facilities.

PRELIMINARY TREATMENT

Preliminary treatment (pretreatment) is defined as those operations performed on the waste stream to make it suitable for introduction into a municipal waste treatment system or a separate industrial on-site secondary wastewater treatment system. The problems will be similar except for the longer sewer lines usually involved in treatment at a municipal plant.

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

1. Removal of pollutants found to pass through a POTW inadequately treated.
2. Removal of causes of treatment system upset or hazards and of collection system obstructions or potentially damaging materials.
3. Effluent criteria.
4. Reduction of load to secondary treatment units.
5. Sludge disposal criteria.

Tannery effluents exhibit a wide range of pollutants and pollutant concentrations. Suspended solids vary from 300 to 14,000 mg/l with an expected average of 2,000-3,000 mg/l[6 15]. The BOD5 of tannery effluents can vary from 150 mg/l to 3,000 mg/l, with an average usually from 1,000 to 2,000 mg/l[6]. Grease concentrations in tannery waste can be as high as 850 mg/l. Sulfide and chromium concentrations also show a wide variation in raw wastes. Normal 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. There appears to be some evidence, according to one author, to indicate that both forms may be toxic[16], however there is considerable uncertainty on this subject. Trivalent chromium salts are soluble in acid and neutral solutions. At a pH greater than 8.5, trivalent chromium will be precipitated. Total chromium concentrations of 20 mg/l or more are indicated as hardly toxic to biological treatment systems[6]. The batch nature of tannery operations creates wide fluctuations in waste flows and waste strengths. Such variations can be difficult to handle, and may result in over- or under-design of the preliminary and secondary treatment units.

Significant reductions in suspended solids and BOD5 and equalization of flows and waste strength may be required to avert overloading of biological treatment units where tannery wastewater is the major contributor to a POTW.

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

1. Screening
2. Equalization
3. Sulfide oxidation
4. Plain sedimentation
5. Chemical treatment
    a. Coagulation and sedimentation
        1) Alum
        2) Lime
        3) Iron salts
        4) Polymers
    b. Carbonation
    c. pH adjustment
6. Sludge handling and disposal

SCREENING

Fine screening removes hair particles, wool, fleshings, hide trimmings, and other large-scale particulates. While reducing undesirable wastewater constituents, screening creates 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 to parameters such as BOD5 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 pretreatment 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, the equalization of flow, strength, and pH of strong liquors may be necessary. 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 should be determined based upon the wastewater generation patterns of the tannery and the requirements of the secondary treatment facility. Basins can be monitored through pH and flow measurement.

An equalization tank or basin is usually of considerable size and most economical at low ratios of height to surface area, subject to the need to conserve the heat content of the wastewater, for more effective biological treatment system operation. Tanneries with insufficient space for such a tank have another option to approximate the same effect of smoothing the hydraulic effluent loading. This option which is being used by at least one tannery is to schedule wastewater dumps from the tanning process facilities in accordance with a wastewater discharge schedule that is designed to smooth the hydraulic loading on the POTW.

SULFIDE OXIDATION

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 not accomplished with plain sedimentation. Sulfides are more satisfactorily removed through oxidation. Various methods for oxidizing sulfides include:

1. Air oxidation.
2. Direct chemical oxidation[9].
3. Catalytic air oxidation[10 9 11].

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

Direct chemical oxidation with ammonium persulfate and ozone was studied by Eye[9]. Ammonium persulfate produced low removals. Ozone was most effective; however, the expense of ozone-generating facilities and developing contact equipment negated further study[9].

Studies by Chen and Morris[11] 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. Chen and Morris[11] found that nickel, cobalt, and manganous ions are all effective and predicted that potassium permanganate would work well. Their best formulations achieve complete removal with short contact times such as 15 minutes. Kessic and Thomsom[12] obtained 95 to 97 percent oxidation of sulfides at short contact times around 20 minutes using manganous ion as the catalyst. These solutions were very dilute and residual sulfide levels between 0.3 and 1.0 mg/l were achieved. In two studies, Veno[13 14], obtained between 92 and 100 percent sulfide oxidation using high temperatures, great excesses of air and many different catalyst systems. Among those found to give good results were ferric sulfate, ferric chloride, activated carbon, carbon black, ammonium peroxydisulfate, and hydroquinone. Eye and Clement[9] found that potassium permanganate plus air, ozone, or manganous sulfate plus air could remove sulfides completely at short contact times between 3 and 30 minutes. In this study a first stage flow reactor removed 80 percent of the sulfide and a second stage batch reactor the rest. An actual tannery waste required 1.5 hours of treatment with potassium permanganate and air. Bailey[10] and Eye[9] further describe the effectiveness of the metallic catalysts. In a laboratory study[9], 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 the 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 immediate oxygen demand exerted in subsequent biological processes, a catalytic oxidation process is proposed for all tanneries with sulfide-bearing wastes.

PLAIN SEDIMENTATION

Plain sedimentation is concerned with the removal of non-flocculating discrete particles and flotable low-density materials such as grease and scum. Tannery wastes have high concentrations of both suspended solids and grease. As was shown in Table VII-1, suspended solids reductions can range from approximately 40 to 90 percent, while reductions in BOD5 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.

Assumed to be typical for plain sedimentation units is the full-scale operation cited by Sutherland[21]. The suspended solids content of a side leather tannery was reduced 69 percent from 1,200 mg/l to 370 mg/l by sedimentation.

Laboratory experiments by Sproul, *et al.*[25] 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 of suspended solids and 35 percent of BOD5. Pilot scale experiments by Sproul, *et al.*[25] show equalization of plant flows followed by plain sedimentation gave suspended solids and BOD5 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 operations at Tannery No. 10 tend to confirm these removals[6]. 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 and brine cured hides per day for hair pulp beamhouse operations followed by chrome tan and finishing. The following average removals resulted[6].

	Influent mg/l	Effluent mg/l	% Removal
Suspended Solids	3,125	945	70
BOD5	2,108	1,150	45
Total Chromium	51	24	53
Total Alkalinity (as CaCO3)	980	718	27
Grease	490	57	90

Table VII-1. Plain Sedimentation

System	Suspended Solids			BOD			Remarks	Reference
	Inf. mg/1	Eff. mg/1	Removal %	Inf. mg/1	Eff. mg/1	Removal %		
Lagoon	---	---	80-90	---	---	80-90	Fill and draw basins with 24-hour capacity.	(17) (18)
Sedimentation tanks, mechanical sludge facilities	900	130	83-88	380	146	40-63	Pretreatment of vegetable tan liquors. Detention time 9-15 hours.	(19)
Sedimentation tanks	1,200	370	69	---	---	---	Detention time 2 hours	(21)
Sedimentation tanks	1,184	680	43	1,046	537	48	Continuous flow (pilot)	(20)
Sedimentation tanks	1,880	461	67	1,285	873	30	Fill and draw (pilot)	(20)

Suspended solids and BOD5 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 precipiate as chromic hydroxide; however, a very small residual is expected. Although chrome removal from the wastewater 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 BOD5 (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 BOD5 (Table VII-1). High chromium removals may result while sulfide concentrations are relatively unaffected. As a unit operation, plain sedimentation has a desirable application in tannery waste 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, BOD5, sulfides, chrome, and alkalinity through flocculation of colloidal particles. Alum, lime, iron salts, and polymers have exhibited satisfactory results. Data in Table VII-2 indicate that suspended solids removals from 50 to above 98 percent and BOD5 reductions of approximately 50 to 99 percent are achieved.

Chemical coagulation followed by sedimentation has been investigated by Sproul, *et al.*[25] at a cattlehide tannery using the chrome process. Raw wastewater analyses indicate concentrations of BOD5 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 VII-2[25]. Other chemical coagulation results were as follows:

Table VII-2 . 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	References
Coagulation-Sedimentation									
Plain Sedimentation, Coagulation, Sedimentation	Alum	1,550	68	96	--	--	90*	Adjustment of pH water $\underline{H_2SO_4}$	22
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.	28
Coagulation, Sedimentation	Lime	918	469	49	1,001	476	52	Continuous flow with lime concentrations of 1,490 mg/l.	20
Coagulation, Sedimentation	Lime	1,980	497	75	1,630	823	49	Fill and draw with lime concentrations of 1,700 mg/l.	20
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).	23
Coagulation, Sedimentation	Iron Salts	--	--	High	--	--	High	Ferric chloride added at concentrations of 2,000-5,000 mg/l.	26
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).	24
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.	29
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 flow which settled quickly.	29
Sedimentation	None	461	267	42	1,560	1,405	10	Settling bed nothing added.	6
Coagulation, Sedimentation	Alum Poly-electrolyte	516	220	57	445	92	79	Full-scale electrophoresis unit.	6
Sedimentation, Grease Flotation	Alum Poly-electrolyte	3,108	1,103	65	14,118	345	98	Full-scale rectangular sedimentation followed by circular.	6
Sedimentation, Carbonation	None	1,766	731	59	2,166	1,238	43	Full-scale four-hour detention.	6

* Oxygen Demand
** Order of Magnitude Values.

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.

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 pretreatment influent are not completely removed in chemical units. Inconsistent removals are indicated in the literature by researchers[9, 25, 27]. With pH adjustment to 8.0 an upper limit on sulfide removal may be 90 percent[25]. Sulfide removal reduces oxygen demand 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, <u>et al.</u>[25] occurred at a pH of 8.0. Precipitation in a pretreatment sedimentation unit is desirable to prevent any potential toxicity in subsequent biological treatment units.

In pilot plant operations described by Howalt and Cavett[28] and also by Riffenburg and Allison[29]

93 and 99 percent removals of color were observed, respectively. The exact mechanism of removal in each of the colloidal regions is not known; a physical-chemical process is presumed.

In a thesis by Hagan[30], 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 the 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[31]. The efficiency is dependent on pH control around 12.

In general, consistent 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_5[6]. Many low removal efficiencies may have resulted from inefficient control of the physical-chemical operations, which require operator attention to be successful.

CHEMICAL TREATMENT--CARBONATION

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_5 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, and continuous operation of the boilers.

Table VII-2 indicates good removals of suspended solids and BOD5 for carbonation in conjunction with coagulation. The BOD5 removals range from 65 to 92 percent, while suspended solids reductions from 79 to 99 percent are recorded.

Field data from Tannery No. 3 indicated high reductions in suspended solids, BOD5, and total alkalinity. Estimated flows from the cattlehide vegetable tannery were 1,700 cu m/day (0.45 mgd). 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 was also used to assist pH control.) The following removals were indicated[31]:

	Pretreatment Influent mg/l	Pretreatment Effluent mg/l	% Removal
Suspended Solids	2,110	100	95
BOD5	1,660	270	84
Total Alkalinity (as $CaCO_3$)	640	0	100

Carbonation is attractive for tannery pretreatment facilities, where carbon dioxide is available at the cost of piping from the plant boilers. Removals are high, under proper operating conditions, for suspended solids and BOD5.

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, lime or sodium hydroxide to lower or raise pH as required. This requires relatively simple chemical feeding equipment with a pH sensing and control system.

SLUDGE HANDLING AND DISPOSAL

A major part of tannery waste treatment involves the handling and disposal of the semi-solid sludges obtained from liquid treatment processes. The most predominant methods of ultimate disposal of tannery waste sludges include 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 centrifugation, vacuum filtration, and pressure filtration. Centrifuges have appeared to meet with less success than vacuum filters or pressure filters.

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 at Tannery No. 11[6], where about 80 percent of the waste flow is tannery waste. Such heat treatment provides a stable end product from a biological standpoint, which can be incorporated into a landfill or spread on the land. One of the principal difficulties with tannery waste is the chromium content in sludges and the potential toxic impact of material on the environment. In testing a heat-treated alkaline 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, high pH, and the 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 lower 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 of chromium or other constituents on plants or, through leaching, on ground or surface water supplies.

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

Use of lagoons, drying beds, landfills, and landspreading all require key attention to the environmental impacts. Particularly important is the leaching of potential toxic or organic materials to the groundwater 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[1].

SECTION VIII

COST, ENERGY, AND NONWATER QUALITY ASPECTS

SUMMARY

Pretreatment cost estimates are reported for various representative size groups within the subcategories of the leather tanning and finishing industry. The plant size division is based on number of hides/skins handled as a raw material. This division of the industry subcategories does not imply the need to categorize according to size. As indicated in Section IV, the categorization rationale does not support a size basis for categorizing the industry. Capital costs, operating costs, and annual costs for waste treatment are usually related to hydraulic loading and there are economies of scale as wastewater volume increases. The cost distribution over greater numbers of hides in larger plants obviously reduces the unit cost contribution of pretreatment for each hide. These differences are significant and single-value average costs for each subcategory irrespective of size would have distorted the cost information.

Wastewater treatment capital cost is primarily a function of total wastewater flow rate. Cost per unit of production for waste treatment will vary with total investment cost and the production rate. Therefore, the subcategory treatment costs have been estimated on the basis of "typical" plants for each size. A "typical" plant is a hypothetical model plant with an average production rate and with a wastewater flow rate as indicated by the data in Table VIII-1. The operating parameters of these model plants are based on information from this study and the study of the economic impact of pretreatment on this industry. Tannery production ranges, in hides/skins per day, were determined for the various plant sizes in the economic impact study on this industry. The midpoint in the range of production specified for each size was used as the "typical" production level for that size plant. Wastewater flow data collected in this study were used to determine typical flow rates per unit of production. The total flow was then calculated by multiplying this latter figure by the average production for each size. The average hide or skin weight is based on the average of the tanneries in each subcategory. The average raw waste load for each subcategory is reported in Section V of this report. The raw waste load per unit weight of hides does not vary significantly with plant size within each subcategory.

Table VIII-1. "Typical" Plant Operating Parameters Used For Estimating Cost of Achieving Pretreatment Standard

Category	Plant Size	Production, Hides/Day	Wastewater Volume		Average Hide or Skin Weight	
			CuM/D	MGD	kg	lb
1 & 2	Extra Small	100	106	0.028	22.3	49
	Small	400	413	0.109	22.3	49
	Medium	900	886	0.234	22.3	49
	Large	1,500	1,400	0.370	22.3	49
	Extra Large	3,000	2,460	0.650	22.3	49
3	Extra Small	100	182	0.048	28.2	62
	Medium	625	719	0.190	28.2	62
	Large	1,500	1,135	0.300	28.2	62
4	Medium	900	885	0.234	32.3	71
	Large	1,500	1,400	0.370	32.3	71
5	Medium-Sides	2,000 sides	424	0.112	12.7	28
	Medium-Splits	4,250 splits	159	0.042	4.5	10
6	Extra Small	1,200 skins	53	0.014	14.1*	31*
	Small	2,400	148	0.039	14.1	31
	Medium	5,800	477	0.126	14.1	31
	Large	5,000 hides	1,135	0.300	14.1	31
7	Extra Small	900 skins	454	0.120	5.0	11
	Small	3,000	1,476	0.390	5.0	11
	Large	5,000	2,460	0.650	5.0	11

*Weighted average of 50 percent cattle hides and 50 percent sheepskin.

A capital investment will be necessary for about 50 percent of the tanneries in the industry to achieve the pretreatment standard, as indicated in Table VIII-2. This investment required of each "typical" plant in the appropriate categories is indicated in Table VIII-3. The distribution indicated in Table VIII-2 is based on information collected from the industry in the course of this study. The estimates of the percentages of tanneries as indicated in Tables VIII-2 and VIII-4 are based on a determination of the pretreatment requirements of each plant in the sample of each category then subtracting the number of plants with adequate facilities in place, as reported in the questionnaires submitted by the tanneries. The numbers of plants determined in this manner were then related to the total number in the sample of each category of the industry as the percentages indicated.

The cost to achieve the pretreatment standard is based on the use of batch catalytic sulfide oxidation. The total cost to the tanning industry is estimated at $7.3 million, distributed as indicated in Table VIII-5, to achieve the draft recommended pretreatment standard. This investment cost related to total annual production of the tanneries involved varies from 17 cents per hide to 35 cents per hide to construct the suggested preliminary treatment system.

The investment cost for the combined pretreatment system is estimated at $12.2 million. This is based upon the potential need in some cases for screening, pH control, and flow equalization in addition to sulfide removal, as judged necessary by the specific tannery location and the circumstances of the affected POTW. The combined system is not required by the draft recommended limitation, but it is suggested as a means of minimizing municipal system problems due to tannery waste and of complying with typical municipal discharge ordinances.

The additions to operating and total annual cost for tanneries implementing sulfide removal for the various sizes and categories are indicated in Table VIII-6. The effect of economies of scale is particularly evident in the difference in unit costs between the extra small and the medium and larger plants.

The total energy consumption for wastewater pretreatment by the leather tanning industry will be insignificant in comparison to the total power consumption for plant operations.

Table VIII-2. Percentage of Tanneries That are Expected to Install Sulfide Removal Equipment

Category	Percentage of Tanneries to Be Using Sulfide Removal
1	75
2	75
3	85
4	1 plant
5	0
6	1 plant
7	1 plant
Total Industry	51

Table VIII-3. Capital Investment Cost Estimate for Each Tannery to Provide Sulfide Removal Technology

Category	Plant Size	Capital Investment Cost January 1976 Dollars Sulfide Removal
1	Extra Small	40,000
	Small	61,000
	Medium	78,000
	Large	91,000
	Extra Large	112,000
2	Extra Small	40,000
	Small	61,000
	Medium	78,000
	Large	91,000
	Extra Large	112,000
3	Extra Small	40,000
	Medium	70,000
	Large	91,000
4	Medium	78,000
	Large	NR*
5	Medium-Sides	NR
	Medium-Splits	NR
6	Extra Small	NR
	Small	NR
	Medium	63,000
	Large	NR
7	Extra Small	63,000
	Small	NR
	Large	NR

* NR means not required by existing tanneries.

Table VIII-4. Percentage of Tanneries That May Install Additional Pretreatment Components

	Percentage of Tanneries Used to Estimate Combined System Costs for Each Pretreatment Component		
Category	Screening	pH Control	Flow Equalization
1	43	6	10
2	43	6	10
3	50	6	0
4	1 plant	0	0
5	77	14	0
6	75	12	0
7	33	50	0

Table VIII-5 . Aggregate Pretreatment Capital Cost Estimate for Leather Tanning Industry

Category	Total Number of Plants	Average Production		Average Total Wastewater Flow, CuM/D (MGD)	Aggregate Capital Cost, $ Millions	
		Hides/D	KGS/D (LBS/D)		Sulfide Removal	Combined System
1-Cat/P/Ch.	73	1750	39,091 (86,000)	1499 (0.396)	4.26	6.5
2-Cat/S/Ch	25	1290	28,636 (63,000)	1310 (0.346)	1.46	2.4
3-Cat/Non-Ch	25	710	20,000 (44,000)	666 (0.176)	1.39	1.7
4-T/T/Blue	3	2530	81,818 (180,000)	1635 (0.432)	0.08	0.1
5-Retan	22	2620	36,591 (80,500)	519 (0.137)	0	0.3
6-NB Tan.	31	2980	13,636 (30,000)	(0.100)	0.06	0.5
7-Shearling	11	1830	9,091 (20,000)	1052 (0.278)	0.06	0.7
Total Tanning Industry	190				7.31	12.2

Table VIII- 6. Increase in Operating and Maintenance Cost and Total Annual Cost for Sulfide Removal to Achieve Pretreatment Standard

Size	Costs, $/Year (¢/Hide)									
	Categories 1 & 2		Category 3		Category 4		Category 6		Category 7	
	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual
Extra Small	11,000 (42)	19,800 (76)	11,000 (42)	19,800 (76)	--	--	--	--	11,000 (4.7/skin)	24,900 (11/skin)
Small	11,000 (11)	24,400 (24)	--	--	--	--	--		--	--
Medium	12,000 (5.1)	29,200 (12)	12,000 (7.4)	27,400 (17)	12,000 (5.1)	29,200 (12)	11,000 (0.7/skin)	24,900 (1.6/skin)	--	--
Large	13,000 (3.3)	33,000 (8.5)	13,000 (3.3)	33,000 (8.5)	--	--	--	--	--	--
Extra Large	19,000 (2.4)	43,600 (5.6)	--	--	--	--	--	--	--	--

The pretreatment requirement will not only minimize sulfide hazards for municipal sewerage system personnel and facilities but will also minimize potential odor problems associated with a sulfide pollutant in wastewater entering publicly owned treatment works (POTW). Chromium and oil and grease removal from tannery waste will occur in properly designed and operated POTW's. If the chromium content of the sludge from such a municipal plant becomes a problem, the municipality may require chromium removal at the tannery. This reduces the problem for the municipality, facilitates the achievement of water quality based chrome limitations, and presumably reduces the total volume of chromium-containing sludge to be disposed of.

"TYPICAL" PLANT

The pretreatment systems applicable to tannery wastewater can be used, if necessary, by all plants in the subcategories of the industry. A hypothetical "typical" model plant was constructed for each size in each subcategory as the basis for estimating investment cost and total annual cost for the application of pretreatment systems. The costs were estimated and, in addition, effluent reduction, energy requirements, and nonwater quality aspects of pretreatment were determined.

The pretreatment is applied on the basis of the plant constructs for each subcategory, as indicated previously in Table VIII-1.

TREATMENT AND CONTROL COSTS

In-Plant Control Costs

The cost of installing in-plant modification and wastewater controls, e.g., waste stream segregation, is primarily a function of the specific plant situation. Building layout and construction will largely dictate what can be done, how, and at what cost. Costs for such modifications are not included in any cost estimates for pretreatment. Therefore, all costs are based upon application of treatment processes to the total combined wastewater volume. Significant economies, however, especially for sulfide oxidation, would be possible for segregated and lower volume, more concentrated waste streams.

Capital Investment Cost Assumptions

The waste treatment system costs are based on the plant production, wastewater flow and BOD5 figures listed previously for "typical" model plants in each subcategory. Investment costs for specific pretreatment components are largely dependent on the wastewater flow or hydraulic load.

The actual component cost estimates are based on unit cost curves. The following assumptions are reflected in the capital costs:

* Costs are expressed in January 1, 1976, dollars.
* Expected accuracy for these conceptual-type estimates is ± 30 to 40 percent.
* All design specifications will be prepared by an outside consulting engineer in accordance with applicable codes.
* Construction work to be performed by outside contractor using union labor and no work to be done by in-plant labor or maintenance people.
* Engineering costs are not included in cost estimates, but the construction contractor's overhead and profit are included.
* No land acquisition cost is included.

The capital investment cost estimates indicated in this report will tend to overstate the actual cost that tanneries will incur in installing the suggested technology. For example, a pollution control consultant to the industry reported that to his knowledge no tannery had used an outside contractor to build waste treatment facilities, but that the facilities at each tannery had been built with in-house labor. This would represent a substantial cost savings. There are numerous other investment cost reductions available to the resourceful tannery in design, construction, and operation of pretreatment technology. These reductions cannot be accurately defined or predicted nor is the effect of them included in the cost data. The intent of this cost information is to present a very conservative cost picture of what is suggested for the industry regarding pretreatment technology.

Tables VIII-7 and VIII-8 present capital cost and operating and maintenance cost estimates for the other pretreatment components in common use by tanneries. Table VIII-9 shows operating and maintenance and annual costs for a combined pretreatment system, including sulfide removal. These costs can be used as resource information by tanneries or

Table VIII-7. Capital Investment Cost Estimate for Each Tannery to Provide Optional Pretreatment Technology

Category	Plant Size	Capital Investment Cost, January 1976 Dollars Optional Combined System, Component and Total Cost Screening	pH Control	Flow Equalization	Total**
1	Extra Small	5,000	NR*	36,000	81,000
	Small	13,000	52,000	75,000	201,000
	Medium	26,000	77,000	120,000	301,000
	Large	41,000	99,000	160,000	391,000
	Extra Large	70,000	130,000	230,000	542,000
2	Extra Small	5,000	NR	NR	45,000
	Small	13,000	52,000	75,000	201,000
	Medium	26,000	NR	120,000	224,000
	Large	41,000	NR	NR	132,000
	Extra Large	70,000	130,000	230,000	542,000
3	Extra Small	7,000	36,000	NR	83,000
	Medium	22,000	70,000	NR	162,000
	Large	33,000	NR	NR	124,000
4	Medium	NR	NR	NR	78,000
	Large	41,000	NR	NR	41,000
5	Medium-Sides	6,000	34,000	NR	40,000
	Medium-Splits	14,000	53,000	NR	67,000
6	Extra Small	3,000	23,000	NR	26,000
	Small	6,000	33,000	NR	39,000
	Medium	15,000	58,000	NR	136,000
	Large	33,000	NR	NR	33,000
7	Extra Small	15,000	58,000	NR	136,000
	Small	41,000	99,000	NR	140,000
	Large	70,000	130,000	NR	200,000

* NR means not required by existing tanneries.

** Total Cost includes sulfide removal where indicated on Table plus combined components listed, therefore is maximum potential cost.

Table VIII-8 . Pretreatment Component Cost Estimates by Category and Size
Capital Cost, Dollars and Operating & Maintenance, Dollars/Year

Plant Description	Wastewater Volume CuM/D, (MGD)	Pump System		Chrome Recycle		Plain Sedimentation		Coagulation Sedimentation		Sludge Treatment, Handling	
		Capital Cost	Operating & Maintenance	Capital Cost	Operating & Maintenance	Capital Cost	Operating & Maintenance	Capital Cost	Operating & Maintenance	Capital Cost	Operating & Maintenance
Categories 1 & 2											
Extra Small	106, (0.028)	30,000	2,900	38,000	1,600	27,000	2,800	25,000	7,900	55,000	7,300
Small	413, (0.109)	40,000	3,200	44,000	3,400	36,000	3,600	56,000	15,000	84,000	10,000
Medium	886, (0.234)	53,000	3,400	47,000	6,100	48,000	4,200	88,000	25,000	110,000	16,000
Large	1400, (0.370)	71,000	3,600	50,000	8,500	57,000	4,600	120,000	35,000	130,000	21,000
Extra Large	2460, (0.650)	100,000	3,800	53,000	14,000	76,000	5,200	170,000	56,000	160,000	33,000
Category 3											
Extra Small	182, (0.048)	32,000	3,000	--	--	29,000	3,200	35,000	9,600	65,000	7,900
Medium	719, (0.190)	50,000	3,400	--	--	43,000	4,100	80,000	21,000	100,000	13,000
Large	1135, (0.300)	64,000	3,500	--	--	52,000	4,400	106,000	30,000	120,000	18,000
Category 4											
Medium	885, (0.234)	53,000	3,400	47,000	6,100	48,000	4,200	88,000	25,000	110,000	16,000
Large	1400, (0.370)	71,000	3,600	50,000	8,500	57,000	4,600	120,000	35,000	130,000	21,000
Category 5											
Medium-sides	424, (0.112)	41,000	3,300	--	--	36,000	3,600	57,000	15,000	58,000	7,400
Medium-splits	159, (0.042)	34,000	2,900	--	--	28,000	3,100	33,000	9,200	46,000	6,400
Category 6											
Extra-Small	53, (0.014)	30,000	2,700	36,000	1,500	25,000	2,700	17,000	6,900	30,000	5,800
Small	148, (0.039)	32,000	2,900	41,000	2,300	28,000	2,900	32,000	9,000	46,000	6,400
Medium	477, (0.126)	43,000	3,300	45,000	4,800	38,000	3,700	64,000	16,000	60,000	7,500
Large	1135, (0.300)	64,000	3,500	48,000	7,500	52,000	4,400	106,000	30,000	120,000	
Category 7											
Extra-Small	454, (0.120)	43,000	3,300	45,000	4,800	37,000	3,600	60,000	16,000	59,000	7,400
Small	1476, (0.390)	71,000	3,600	50,000	8,500	60,000	4,800	124,000	36,000	135,000	23,000
Large	2460, (0.650)	100,000	3,800	53,000	14,000	76,000	5,200	170,000	56,000	160,000	33,000

Table VIII-9. Increase In Operating and Maintenance Cost and Total Annual Cost for Combined Pretreatment System Comprising Components Indicated in Table VIII-4

	Costs, $/Year (¢/Hide)											
	Categories 1 & 2		Category 3		Category 4		Category 5		Category 6		Category 7	
Size	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual	Operation & Maintenance	Total Annual
Extra Small	20,200 (78)	44,200 (170)	20,700 (80)	39,000 (150)	--	--	--	--	7,300 (2.3)	13,000 (4.2)	24,800 (11)	54,700 (23)
Small	26,600 (26)	70,800 (68)	--	--	--	--	--	--	9,000 (1.4)	17,600 (2.8)	24,400 (3.1)	55,200 (7.1)
Medium	37,200 (16)	103,400 (44)	28,500 (17)	34,100 (39)	12,000 (5.1)	29,200 (12)	9,200 (0.8/split)	18,000 (1.6/split)	24,700 (1.6)	54,600 (3.6)	--	--
Large	47,200 (12)	133,200 (34)	19,500 (5)	46,800 (12)	6,700 (1.7)	15,700 (4)	13,000 (2.5/side)	27,700 (5.3/side)	6,500 (0.5)	13,800 (1.1)	36,100 (1.5)	80,100 (3.3)
Extra Large	71,100 (9.1)	190,300 (24)	--	--	--	--	--	--	--	--	--	--

municipalities considering the use or the requirement of such pretreatment facilities. These costs are based on the same assumptions as described previously.

Annual Cost Assumptions

The components of total annual cost are capital cost, depreciation, and operating and maintenance costs which include energy and power costs. The cost of capital is estimated to be twelve percent of the investment cost. This cost is an estimate of the weighted average of the cost of equity and of debt financing throughout the industry. Operating and maintenance cost includes all the components of total annual cost except cost of capital and depreciation.

The depreciation component of annual cost was estimated on a straight-line basis, with no salvage value and a ten-year life for all capital investment costs.

The labor rate for O&M man-hours was set at $5.00 per hour plus 50 percent for burden, supervision, etc., based on information from the industry. Electrical power cost was estimated to be 2.5 cents per kw-hr. Other costs, including materials and supplies are based on additional unit cost curves. The operating year was assumed to be 260 days per year in all cost calculations to account for the variable numbers of days per week reported by the industry--5, 5.5 and 6.

ENERGY REQUIREMENTS

The energy requirements 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, tanyard, and finishing operations.
3. Degree of mechanization within the industry.
4. Climate of the tannery location.

Energy requirements for a typical cattlehide-chrome tannery processing hides from raw material to finished product are approximately 0.46 kw-hr/kg of hide (0.21 kw-hr/lb) of electrical energy and 3,560 kg cal/kg of hide (6,700 Btu/lb) for steam. The energy requirements for sulfide removal approximate five to ten percent of the total plant electrical energy and less than one percent of the total plant energy requirement[1].

NONWATER POLLUTION BY WASTE TREATMENT SYSTEMS

Solid Wastes Characteristics. Solid waste from a tannery with a wastewater pretreatment/treatment system may include any or all of the following:

* Fleshings
* Hair
* Hide trimmings
* Tanned hide trim and shavings
* Leather trimmings
* Buffing dust
* Leather finishing residues
* Wastewater treatment sludges
* General plant waste

The specific types of solid waste generated by a tannery depend upon the type of processing operations conducted, and the quantity of each type of waste generated depends upon the volume of production at the tannery.

Tanneries which generate fleshings and hide trimmings normally sell these waste materials to rendering plants, or occasionally to glue manufacturers. Since these waste materials are highly putrescible, daily collection is required. Very small tanneries which process only a few hundred hides per day often find it uneconomical to sell this waste since the by-product recovery value is exceeded by the handling and transportation costs.

Most vegetable leather tanneries and a few chrome leather tanneries remove hair from hides using a hair-save operation. At these tanneries, the hair is washed, dried and baled, and subsequently sold as a by-product. Use of the hair-save method is declining in favor of the hair-burn method. As noted in Section III, however, some tanners still use a modified hair-save beamhouse which produces hair that is disposed of in a landfill. At tanneries using the hair-burn method of hair removal, the hair is dissolved and becomes part of the wastewater stream.

Some chrome leather tanneries which generate large quantities of tanned hide trimmings and shavings, particularly split leather tanners located in the northeastern U.S., are able to sell this waste material as a by-product. By-product uses include manufacture of fertilizer, chrome glue, hog feed supplement, or leather board. The majority of this type of waste, however, is disposed as solid waste.

A recent study estimated that the total quantity of land-disposed solid waste generated by the leather tanning and finishing industry in 1974 was 203,000 metric tons[32]. The distribution of the total quantity of waste between the four major waste types was as follows:

Type of Waste	Quantity*	Percent of Total Waste
Wastewater pretreatment/ treatment residues (screenings & sludge)	122,000	60
Tanned hide trimmings & shavings and leather trimmings	71,000	35
General plant waste	6,000	3
Leather finishing residues	4,000	2

*metric tons generated in 1974

<u>Treatment and Disposal</u>. Approximately 60 percent of the wastewater treatment residues produced come from chrome leather tanneries with primary and/or secondary wastewater pretreatment/treatment facilities, 20 percent from chrome tanneries with secondary wastewater treatment systems. Primary and/or secondary treatment sludge from chrome tanneries is normally dewatered prior to disposal. Sludge dewatering may be accomplished using gravity or mechanical means. Gravity dewatering (sequential settling) is relatively uncommon; however, sludge drying beds on the tannery plant site are used by some tanners. Mechanical sludge dewatering is normally accomplished using vacuum filters, centrifugtes, or filter presses. These three mechanical dewatering techniques have all been found to be effective in producing sludge cakes ranging approximately from 10 to 40 percent solids. There seems to be a preference for filter presses due to the slightly drier (40 percent solids) filter cake produced.

Secondary wastewater treatment sludges from vegetable tanneries are normally dewatered in evaporative lagoons, after which the sludge is used as a soil conditioner or disposed of in a dump or landfill.

Sewer sump sludge is composed primarily of precipitated lime and is not normally dewatered prior to disposal. Dumps and landfills are the most common disposal facilities for this waste.

Sixteen landfills which receive tannery wastes were visited during a recent EPA-sponsored study[32]. Most of the operators interviewed indicated that dewatered tannery wastewater pretreatment/treatment sludge could be handled adequately. Appropriate handling was reported to involve mixing the sludge with domestic refuse in proportions which would allow the combined material to be worked by normal landfill equipment.

The different types of solid waste disposal facilities utilized and estimates of the proportion of the total quantity of tannery solid waste going to each type of facility are shown in Table VIII-9. As shown, nearly all tannery solid waste is disposed in landfills or dumps. Trenches, lagoons, and certified hazardous waste disposal facilities are currently used almost exclusively for sludge disposal. A small percentage of tanneries operate their own disposal sites. Tannery-owned disposal facilities are usually associated with vegetable leather tanneries and are the result of the plant's remote location or the fact that other disposal sites will not accept the waste (usually sludges).

Most tannery solid waste which is land disposed contains substantial concentrations of trivalent chromium (up to several percent on a wet weight basis), and in many cases, copper, lead, and zinc as well. For example, the "typical" concentrations of certain constituents in tannery sludge are presented in Table VIII-10. As shown, sludge from vegetable leather tanneries is the only type which does not normally contain significant heavy metal concentrations.

The possibility that leachate generation and subsequent contamination of ground and surface waters may occur at facilities where tannery wastes are disposed of requires that disposal sites be carefully selected. Site topography must minimize surface water flow across the site and the soils should be able to contribute to leachate attenuation. Operational procedures should be employed which will minimize percolation of precipitation through the refuse. Leachate collection systems at landfills used for solid waste disposal are recommended to provide adequate assurance that ground and surface waters will be protected from contamination.

Leather finishing residues are the one solid waste from tanneries that may contain significant quantities of flammable organic solvents. Consequently, disposal sites which receive this type of waste need to take precautions to minimize the potential fire hazard from this material. The quantities of this type of waste which are generated are small enough that land disposal is thought to be an environmentally adequate disposal alternative.

Table VIII-10. Disposal Sites Utilized

General Category of Disposal Site	Specific Type of Disposal Site	Percent of Waste Disposed
Landfill		60
	municipal sanitary	3
	private sanitary	3
	municipal engineered*	5
	private engineered	10
	municipal converted**	20
	private converted	14
	on-site tannery	5
Dump		25
	municipal	20
	private	1
	on-site tannery	4
Trenches or lagoons		9
	municipal	4
	private	4
	on-site tannery	1
Certified***	private	6

*Engineered disposal sites which do not provide daily cover
**Dumps which have been coverted to landfills without being engineered
***Certified hazardous waste disposal facilities

Table VIII-11. "Typical" Sludge Characteristics*

Constituent	Chrome leather tannery pretreatment/treatment sludge before dewatering	Chrome leather tannery pretreatment/treatment sludge after dewatering	Chrome leather tannery sewer sump sludge (not dewatered)	Vegetable leather tannery secondary treatment sludge (not dewatered)
Solids content (%)	5-10	20-30	5-15	3-6
Chromium (mg/l)	3,000-6,000	10,000-15,000	2,000-4,000	<5
Copper (mg/l)	100-150	150-200	100-200	<10
Lead (mg/l)	10-25	50-150	10-25	<5
Sulfides (mg/l)	20-50	50-150	30-60	25-50
Phenols (mg/l)	<10	<10	<10	<1

*All values are on a wet weight basis

Air Pollution

Particulate matter and hydrogen sulfide are the two potential causes of air pollution from leather tanning and finishing processes. Hydrogen sulfide is toxic even in low concentrations and is the main cause of odors in tannery waste treatment systems. Hydrogen sulfide is formed principally by reactions involving sulfide wastes from the unhairing process. The pretreatment standard requires sulfide removal prior to discharge to municipal sewers and treatment. This should eliminate any air pollution problems that could result from sulfides and improve the potentially lethal working conditions of workers in and around municipal treatment systems.

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 oil-fired 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 wastewater 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.

Noise

The most significant increase in noise due to waste treatment is that from large pumps and air compressors. When such a system is housed in a low-cost building, the noise generated is confined within the building, but the noise may be amplified to high levels in the building by such installation practices. All air compressors, air blowers, and large pumps in use on intensively aerated treatment systems, and other treatment systems as well, may produce noise levels in excess of the Occupational Safety and Health Administration standards. The industry must consider these standards in solving its waste problems.

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE--EFFLUENT LIMITATIONS GUIDELINES

To be added later.

SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE-- EFFLUENT LIMITATIONS GUIDELINES

To be added later.

SECTION XI

PRETREATMENT STANDARDS

INTRODUCTION

The effluent limitations that must be achieved by facilities in the leather tanning and finishing industry that discharge into a municipal sewerage system for treatment in a publicly owned treatment works (POTW) are termed pretreatment standards. These standards are determined by identifying the reduction necessary for effluent constituents that would interfere with, pass through, or otherwise be incompatible with a properly designed and operated POTW.

Consideration was also given to the following in establishing a pretreatment standard:

* The total cost of application of technology in relation to the effluent reduction and other benefits to be achieved from such application;
* The size and age of equipment and facilities involved;
* The processes employed;
* The engineering aspects of the application of pretreatment technology and its relationship to POTW's;
* Process changes;
* Nonwater quality environmental impact (including energy requirements).

Pretreatment standards must reflect effluent reduction achievable by the application of primary treatment technology as used in the industry and by-in-plant controls when such are considered to be normal practice within the industry.

A final consideration is the determination of economic and engineering reliability in the application of the primary or pretreatment technology. This must be determined from the results of demonstration projects, pilot plant experiments, and, most preferably, general use within the industry.

EFFLUENT REDUCTION ATTAINABLE BY PRETREATMENT TECHNOLOGY

Information presented in Sections III through VIII of this report and organized and summarized in this section leads to a determination that the necessary effluent reduction attainable by pretreatment technology in the leather tanning and finishing industry shall result in sulfide removal from all tannery wastewaters.

IDENTIFICATION OF PRETREATMENT TECHNOLOGY

The pretreatment technology to be used by leather tanning and finishing plants to achieve the pretreatment standard is catalytic oxidation in a batch mixing/reaction tank. The predominant industry practice in implementing this technology involves manganous sulfate as the catalyst in a steel or concrete tank equipped with a compressed air aeration system.

As pointed out in Section VII, additional wastewater management and control practices which should be considered by tannery management to reduce wastewater volume, pollutant loading, and concomitantly the surcharges and capital cost recovery paid, include the following:

* Appoint a person with specific responsibility for water management. This person should have reasonable powers to enforce improvements in water and waste management.
* Determine or estimate water use and waste load strength from principal sources. Install and monitor flowmeters in all major water use areas.
* Segregate waste streams from each major in-plant process, i.e., beamhouse, tanyard, and retan/finishing for subsequent treatment before mixing with others.
* Collect unhairing waste stream, reduce pH to isoelectric point to precipitate and dissolve protein, and recover the protein as a valuable by-product.
* Reuse, or recover active chemicals for reuse from waste streams such as the sulfide containing stream, pickling solution, chrome tanning solution.
* Provide regularly scheduled maintenance attention for screening and solid waste handling systems throughout the operating day. A back-up screen may be desirable to minimize solids entry into the municipal waste treatment system.
* Use more care in unloading, unfolding and otherwise preparing hides for first process step to minimize salt entry into the sewers.
* Make all employees aware of good water management practices and encourage them to apply these practices.

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* Collect unhairing waste stream, reduce pH to isoelectric point to precipitate and dissolve protein, and recover the protein as a valuable by-product.
* Reuse, or recover active chemicals for reuse from waste streams such as the sulfide containing stream, pickling solution, chrome tanning solution.
* Provide regularly scheduled maintenance attention for screening and solid waste handling systems throughout the operating day. A back-up screen may be desirable to minimize solids entry into the municipal waste treatment system.
* Use more care in unloading, unfolding and otherwise preparing hides for first process step to minimize salt entry into the sewers.
* Make all employees aware of good water management practices and encourage them to apply these practices.

Such practices are feasible and may be economically attractive by reducing municipal water and sewage charges because of lower flows and waste loadings.

RATIONALE FOR THE PRETREATMENT STANDARD

The rationale for the decision on the pretreatment standard rests primarily on the definition of incompatible as used in Section 307(b) of the Act and as it applies to the waste contaminants in the raw wastewater from leather tanneries. Incompatible pollutants are specifically defined in the Act as those pollutants which either interfere with or pass through inadequately treated. Among the pollutants in the raw waste from tanneries, BOD5, TSS, oil and grease, total chromium, sulfide, and ammonia, are present in sufficient concentrations to represent potential problems for POTW's. Within this technology based analysis, it was assumed that any joint municipal-industrial POTW will include primary and secondary treatment which is properly designed and operated to effectively treat its unique mixture of domestic and industrial wastewaters, including adequate consideration of the specific characteristics of industrial wastewaters present, such as those characteristics of trannery wastewater.

The data and information gathered during this study indicate that the BOD5 and TSS found in tannery wastewater are compatible with properly designed and operated secondary biological treatment (i.e., activated sludge). Operating data from four joint municipal-industrial POTW's treating more than 50 percent tannery wastewater indicates that influent BOD5 and TSS concentrations, which range from 250 mg/l to 950 mg/l and 200 mg/l to 900 mg/l, respectively, can be reduced to effluent concentrations of 10 mg/l to 65 mg/l and 11 mg/l to 75 mg/l, respectively. The broad range of influent concentrations did not indicate a sensitivity to a maximum level beyond which the wastewaters were not effectively treated, and therefore no specific treatment of BOD5 or TSS is required to ensure good performance.

Similarly, oil and grease found in tannery wastewaters were found to be removed to low levels, presumably by a combination of skimming in primary clarifiers and biological oxidation in secondary treatment facilities. The performance of one POTW which had extensive data indicated a typical influent oil and grease concentration of 93 mg/l and an effluent concentration of 4 mg/l. Therefore, considering this performance and the nature of the oil and grease being discharged (i.e., primarily animal and/or vegetable origin) no pretreatment limitation is necessary.

There was no evidence found in the data collected from municipalities treating tannery waste or in data from the industry that chromium interferes with the performance of biological treatment systems in use as secondary treatment. The same data reveal that chromium is removed to very low effluent concentrations from wastewater in POTW's which include primary treatment and secondary biological treatment systems.

Evidence in the record indicates that removal of total chromium to very low levels is independent of influent concentration. Optimum removal of chromium in primary clarifiers occurs at a pH of 9 or slightly higher. Residual chromium is removed with waste activated sludge producing effluent concentrations in many cases of 1 mg/l or less of total chromium, which is within NPDES permit conditions where total chromium is not based upon water quality constraints. No other indication of chromium incompatibility is evident from the data and information collected on POTW operation.

The hazardous nature of hexavalent chromium is generally accepted. The use of this type of chrome was found in only two tanneries of about 100 in the sample. These tanneries use the older "two bath" tanning method as described in Section III. As noted in that description, hexavalent chromium is reduced in the tanning drums and therefore should be present in only trace amounts in the wastewater, which also presents a chemically reducing environment due to the presence of significant amounts of organic matter. The data available from all sources indicated hexavalent chromium if present to be in only trace amounts, but usually not at all. The actual presence of hexavalent chrome in tannery wastewater is difficult to quantify very accurately because of the character of tannery wastewater and because no acceptable analytical procedure is available for hexavalent chrome determination for tannery wastewater.

Sulfide is removed in secondary biological treatment systems such as employed in POTW's. However, sulfide can interfere with the operation of POTW's in three significant ways:

1. Sulfides react in wastewater streams, sewers, and POTW components at a certain pH to form hydrogen sulfide which has a threshold limit value of 10 ppm in air. Reports occur periodically about the deaths of workers in sewers, usually caused by hydrogen sulfide poisoning. Similar reports on the deaths of two workers were noted in public record during the course of this study. These accidents can

occur in the confined spaces of the sewer system and in low protected spaces in the municipal treatment plant. This is a totally unacceptable interference that cannot be tolerated.

2. The hydrogen sulfide produced from contaminant sulfides in wastewater can be oxidized to sulfuric acid which is highly corrosive to sewers and treatment plant equipment, shortening their operating life and creating maintenance problems and downtime when the system is not able to operate as needed. This effect also seems to fit as an interference.
3. Sulfides produce hydrogen sulfide odors under certain fairly common conditions in waste treatment processes. These are very obnoxious odors and people are able to smell very low concentrations in air. Chronic odor problems from a POTW may lead to serious problems if local people are frequently exposed to them. Temporary to permanent shut down of the POTW may be the solution to such a problem. This is surely an interference.

Effluent data from POTW's indicates that ammonia nitrogen passes through both POTW's and separate tannery wastewater treatment systems which are well designed and operated. No logical explanation or self evident deficiency could be found to account for this phenomenon. Effluent ammonia concentrations of 100 mg/l or more have been found. However, there is no end-of-pipe pretreatment technology which is practicable and readily available to remove ammonia. In-plant control methods are not readily available either since acceptable substitutes for ammonia compounds in the bating process have not been found. Therefore, while the problem of inadequate treatment of ammonia is recognized, there is no technical or cost effective basis for an ammonia pretreatment limitation at this time. However, this problem will be addressed within the context of the 1983 BATEA revision study.

SIZE, AGE, PROCESSES EMPLOYED, LOCATION OF FACILITIES

The processes employed in different size tanneries within each subcategory are basically similar. Furthermore, the factors of size, age, and processes employed do not affect the pretreatment control technology used and proposed. Hence these factors were not directly involved in determining the pretreatment standard. Also, the location of facilities was not a factor to be considered regarding pretreatment, just as described in Section IV, Categorization.

TOTAL COST OF APPLICATION IN RELATION TO EFFLUENT REDUCTION BENEFITS

Based on information contained in Section VIII of this report, the total investment cost to the leather tanning industry to implement pretreatment is estimated to be $7.3 million. Assuming achievement of 1 mg/l of sulfides by pretreatment, the reduction in the pollutant loading entering POTW's would total about 2.46 million kgs (5.4 million lbs) per year of sulfides. The capital investment cost of such a reduction amounts to $2.97 per kg of sulfide ($1.35 per lb), calculating this figure on the basis of the sulfide reduction that would occur in one year. Potential life savings, protection of public property, and reduction in maintenance costs are other benefits to be derived from implementing the pretreatment standard for which it is difficult or impossible to assign a monetary value.

ENGINEERING ASPECTS OF PRETREATMENT TECHNOLOGY AND RELATIONSHIP TO PUBLICLY OWNED TREATMENT WORKS

The requirements of publicly owned treatment works (POTW's) concerning influent wastewaters should be based on the effluent limits specified by their respective discharge permits, on the type of treatment system and specific facilities available in the POTW, and on the mix of industrial, commercial, and residential dischargers in their sewerage system. These requirements should be embodied in the municipal ordinances governing discharges into the municipal sewers. However, municipal sewer ordinances now in use are based on four primary sources:

* Cincinnati model ordinance,
* Consulting engineer's recommendation,
* Ordinance of another nearby community,
* Stringent NPDES permit requirements.

Rarely is the ordinance based on an assessment of the industrial dischargers' contribution relative to the POTW capability, except for a couple of large sanitary districts and municipalities with significant tannery waste to be treated. However, ordinances of numerous municipalities with tannery waste are currently being reconsidered and rewritten to reflect their specific needs and requirements. Enforcement of any sewer ordinance will probably continue to be a problem. Most municipalities, with some exceptions, will continue to rely primarily on self-policing by industrial dischargers.

There are also a number of instances of specific requirements or allowances involving tannery waste discharges into municipal systems. These decisions have been made at the local level where consideration of many relevant factors has been taken into account. The effluent requirements imposed on the POTW are not compromised and frequently an optimum economic balance for the overall pretreatment-collection-treatment system is achieved.

The engineering aspects of pretreatment technology involve consideration of POTW discharge limitations and treatment capability relative to incompatible pollutants, raw waste characteristics of the industry, and effectiveness of pretreatment technology. There are two pollutants in leather tannery wastewater that require discussion in the context of engineering aspects of pretreatment technology as defined above--chromium and sulfides.

Chromium was formerly purchased by tanneries in the hexavalent form, reduced to the trivalent form in the plant and then used as the tanning agent. Chromium now is almost universally purchased in the trivalent form by leather tanneries. Hexavalent chrome is highly toxic to most life forms at low concentrations in wastewater. The tanning industry is aware of this and has shifted its use of chrome to the trivalent form.

Alkaline precipitation of chromium occurs readily. Chromium removal also occurs in secondary biological treatment systems. Monitoring for chrome in municipal treatment plant effluent is not nearly as extensive as for BOD5 and TSS. Two factors impact on the chrome concentration of POTW effluent. First, dilution by other wastes entering the POTW occurs, then removal occurs within the waste treatment processes.

During this study, contacts were made with about 40 municipal treatment superintendents or plant operators and no operational or other problems were reported with chromium in the influents to their plant or in their effluent.

Chromium is not an incompatible pollutant for a POTW. A decision to set no pretreatment limit for chromium does shift the chromium-containing sludge load to the POTW. This results in a greater quantity but lower concentration of chromium-containing sludge to be handled and disposed by the municipality instead of the tannery.

One municipality, however, did indicate the intention to establish a total chromium pretreatment limitation due to problems in finding an acceptable landfill site for chromium-containing sludges.

Most municipal sewer ordinances collected during this study from cities with a tannery discharge into the municipal system specify, "...no toxic or hazardous materials in sufficient quantity to cause problems..." or similar phrase. Of thirty ordinances received, two specify a sulfide limit of 10 mg/l and three a limit of 1 mg/l. Sulfides are removed by POTW secondary treatment processes. However, the substantial hazards of life and property that sulfides in wastewater potentially represent establish sulfides as incompatible, commensurate with the intent of the Act.

Several sources in the literature, as indicated in Section VII, describe the oxidation of sulfides as an effective removal technology, especially applicable to tannery wastewater. Catalytic oxidation is reportedly highly effective with acceptable and economical time requirements. Such oxidation approaches 100 percent removal. The literature sources frequently indicate the reduction of sulfides to zero or indicate 100 percent removal without specifying a minimum or limiting low level concentration, which the oxidation systems may in practice, only approach. The implication of these statements in the literature seem to be less than 1 mg/l for a sulfide concentration in wastewater after sulfide oxidation. There is no limiting low level concentration reported for an oxidation process in this literature. Effluent reduction reported as a percent must be related to influent level to comprehend the meaning and significance of the reduction reported. A percentage reduction may be related to influent level and/or removal of a specific quantity of pollutants. The time requirement for an oxidation process will also depend on the total weight of pollutant material loading.

Raw waste sulfide concentrations are known for 21 leather tanning plants and sufficient data is provided to identify the high/low and typical concentrations for each plant and for the entire group of 21 plants as indicated in Table XI-1. The average maximum concentration is 101 mg/l, and the average of the minimum concentrations is 5.3 mg/l.

The average raw waste sulfide concentration among the 21 plants is 42 mg/l and the median is 44 mg/l. Two plants have average sulfide concentrations of less than 1 mg/l and seven of the 21 plants in the sample report minimum sulfide concentrations of less than 1.0 mg/l. Effective pretreatment is being achieved by the industry.

IN-PLANT CHANGES

The primary in-plant change that would significantly affect waste treatment system requirements is waste stream segregation.

Table XI-1. Sulfide Concentrations of Tannery Wastewater

Plant	Sulfide Concentrations, mg/l	
	Average	Range
A	135	53 - 219
B	66	33 - 98
C	45	5.3 - 196
D	49	8.7 - 99
E	15	7.6 - 38
F	4.8	0.16 - 17
G	0.66	0.08 - 1.6
H	944	135 - 5016
I	44	8 - 104
J	41	0.14 - 300
K	142	26 - 256
L	20	3 - 49
M	47	16.8 - 102
N	44	35 - 54
O	56	4.0 - 218
P	34	7 - 52
Q	9.4	1.7 - 20
R	85	0.05 - 150
S	6.2	0.05 - 38
T	4.4	0 - 8.4
U	0.02	0 - 0.05
Overall	42.5	16.4 - 101
Median	44	5.3 - 99

This results in smaller volumes and usually more economical treatment than is possible after all wastes have been mixed creating a larger volume and lower concentrations. Waste stream segregation is ideally suited and used in tanneries on the beamhouse and tanyard wastes. Other recycle, reuse, and recovery techniques that can be implemented within tannery operations can reduce total wastewater volume, pollutant loading, chemicals consumption, and perhaps produce a by-product of value.

NONWATER QUALITY ENVIRONMENTAL IMPACT

The proposed pretreatment standard will substantially reduce the potential hazards to life and property in sewerage systems and POTW's and the potential for odor problems in the operation of the POTW from the sulfide bearing wastewaters from tanneries.

Most landfill operators interviewed during a recent EPA-sponsored study[2] indicated that dewatered tannery wastewater pretreatment/ treatment sludge could be handled adequately. Appropriate handling was reported to involve mixing the sludge with domestic refuse in proportions which would allow the combined material to be worked by normal landfill equipment.

However, the possibility that leachate generation and subsequent contamination of ground and surface waters may occur at facilities where tannery wastes are disposed of requires that disposal sites be carefully selected. Site topography must minimize surface water flow across the site and the soils should be able to contribute to leachate attenuation. Operating procedures should be employed which will minimize percolation of precipitation through the refuse. Leachate collection systems at landfills used for solid waste disposal are recommended to provide adequate assurance that ground and surface waters will be protected from contamination.

SECTION XII

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SECTION XIII

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SECTION XIV

GLOSSARY

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.

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.

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 in 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.

Blue

The state or condition of hides subsequent to chrome tanning and prior to retanning. Hides in this stage of processing are characteristically blue in color.

Buffing

A light sanding operation applied to the grain or underside of leather and also to splits. Buffing smooths the grain surface and improves the nap of the underside of the leather.

Buffing Dust

Small pieces of leather removed in the buffing operation. Buffing dust also includes small particles of abrasive used in the operation and is of a coarse powder consistency.

Carding

Method using a wire brush to disentangle wool. One of the shearling finishing processes.

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 in 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 in 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 wastewater 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.

Combination Tanned

Leathers tanned with more than one tanning agent. For example, initially chrome-tanned followed by a second tannage (called a RETAN) with vegetable materials.

Composite Sample

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

Concrete Mixer

A term often applied to hide processors.

Conditioning

Introduces controlled amounts of moisture to the dryed leather giving it varying degrees of softness.

Corium

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

Degreasing

In pigskin and sheepskin tanneries a solvent or detergent is added to the drum containing washed hides. Grease is removed from the hides and recovered as a by-product.

Deliming

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

Demineralization

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

Dermis

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 dwelling time of wastewater in a treatment unit.

Dewatering

The process of removing 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.

Dry Milling

The rotating of leather in a large wooden drum with no added chemicals or water. Dry milling softens the leather.

Electrodialysis

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

Embossed

A mechanical process of permanently imprinting a great variety of unique grain effects into the leather surface. Done under considerable heat and pressure.

Enzymes

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 outgrowth.

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.

Equivalent Hides

A statistical term used by the Tanners' Council of America to relate the production of tanneries using various types of raw materials. An equivalent hide is represented by 3.7 sq m of surface area and is the average size for a cattlehide.

Eutrophication

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

Fatliquoring

A process by which oils and related fatty substances replace natural oils lost in the beamhouse and tanyard processes. Regulates the softness and pliability of the leather.

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.

Fleshing

The mechanical removal of flesh and fatty substances from the underside of a hide prior to tanning. In the case of sheepskin tanning, fleshing is often accomplished after the tanning process.

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 wastewater 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 is 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 is 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 in mg/l.

Green Hides

Hides which may be cured but have not been tanned.

Head

That part of the hide which is cut off at the flare into the shoulder; i.e., the hide formerly covering the head of the animal.

Hide

The skin of a relatively large animal, at least the size of mature cattle.

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 the 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.

Nitrogen, Ammonia

A measure of the amount of nitrogen which is combined as ammonia in wastewater. 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 wastewater. Expressed in 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 wastewater or other drainage is discharged into an ocean, lake, or river.

Pack

Layers of salted hides formed at the slaughterhouse 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 logarithm of the hydrogen ion concentration in wastewater expressed as a standard unit.

ppm

Parts per million. The expression of concentration of constituents in wastewater, 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 a smooth plate with a starch and water paste and dried in a controlled heated vessel.

Pickling

The process that follows bating whereby the hide is immersed in a brine and acid solution to bring the skin or hide 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. Plating may be done with an embossing plate which imprints textured effects into the leather surface.

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.

POTW

Publicly owned treatment works, i.e., municipal waste treatment system.

Pullery

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

Pulp

Method of unhairing in which depilatory agents are used to dissolve hair entirely in a few hours.

Retanning

A second tanning process utilizing either the natural tanning materials (chromium or vegetable extracts) or synthetic tanning agents. Retanning imparts specialized properties to the leather.

Reverse Osmosis

A process whereby water is forced to pass through semipermeable 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.

Sedimentation

Clarification (settling).

Setting Out

A multi-purpose operation which smoothes and stretches the skin while compressing and squeezing out excess moisture. Puts hides into proper condition for drying.

Sharpeners

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

Shaving

An abrasive, mechanical action used to correct errors in splitting and thus yielding a uniformly thick grain side or split.

Shavings

The waste products generated during the shaving operations. These are essentially small pieces of the tanned hide, which are approximately the size of wood shavings.

Shearling

A lamb or sheepskin tanned with the hair retained.

Shoulder

That part of the hide between the neck and the main body of the hide.

Side

One-half of a hide, produced by cutting the hide down the backbone. Normally done to facilitate processing using smaller equipment than would be required if full hides were processed.

Skin

The pelt or skin of animals smaller than mature cattle; e.g., pigskin, sheepskin, calfskin.

Skiver

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 non-uniform thickness called a split.

Staking

Mechanically softens the leather by stretching and flexing it in every direction. Usually done on automatic machines which move leather between rapidly oscillating, overlapping fingers.

Sulfide

Ionized sulfur. Expressed in mg/l as S.

Suspended Solids (SS)

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

Syntan

Synthetic tanning materials, generally used in combination with vegetable, mineral, or formaldehyde tannages. Syntans are almost exclusively used in retanning rather than tanning operations.

Tannin

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

Tanyard (Tanhouse)

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

Toggling

Method of drying in which skins are kept in a stretched position by means of clips called toggles. The skin is attached to a perforated frame which is slid into a drying oven.

Total Dissolved Solids (TDS)

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

Total Solids (TS)

The total amount of both suspended and dissolved materials in wastewater. Expressed in mg/l.

Trimming

The removal of the ragged edges and inferior portions of hides and skins either before or after tanning. Trimming is normally accomplished by workers using knives.

Trimmings

The hide and leather scraps produced during the trimming operation.

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.

CONVERSIONS

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	kilowatts
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