

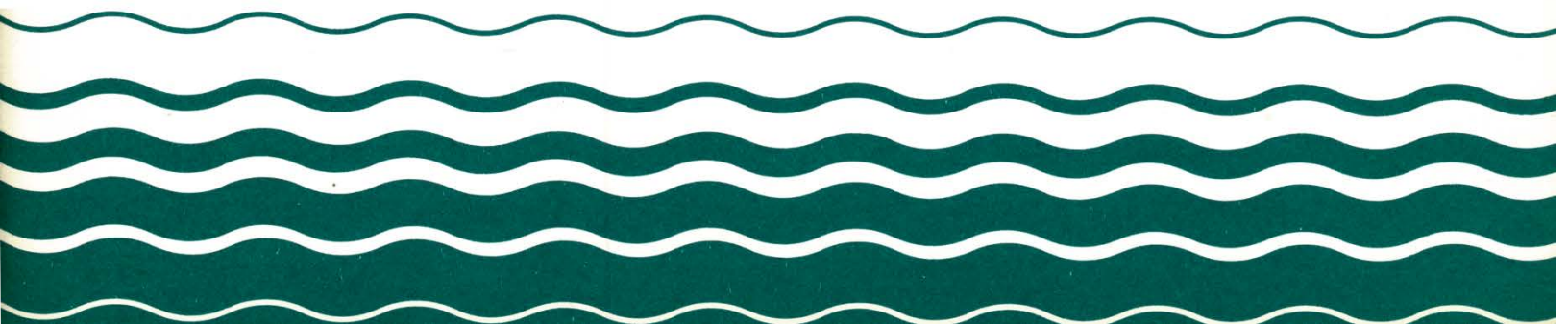
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Water

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# **Guidance Manual for Leather Tanning and Finishing Pretreatment Standards**



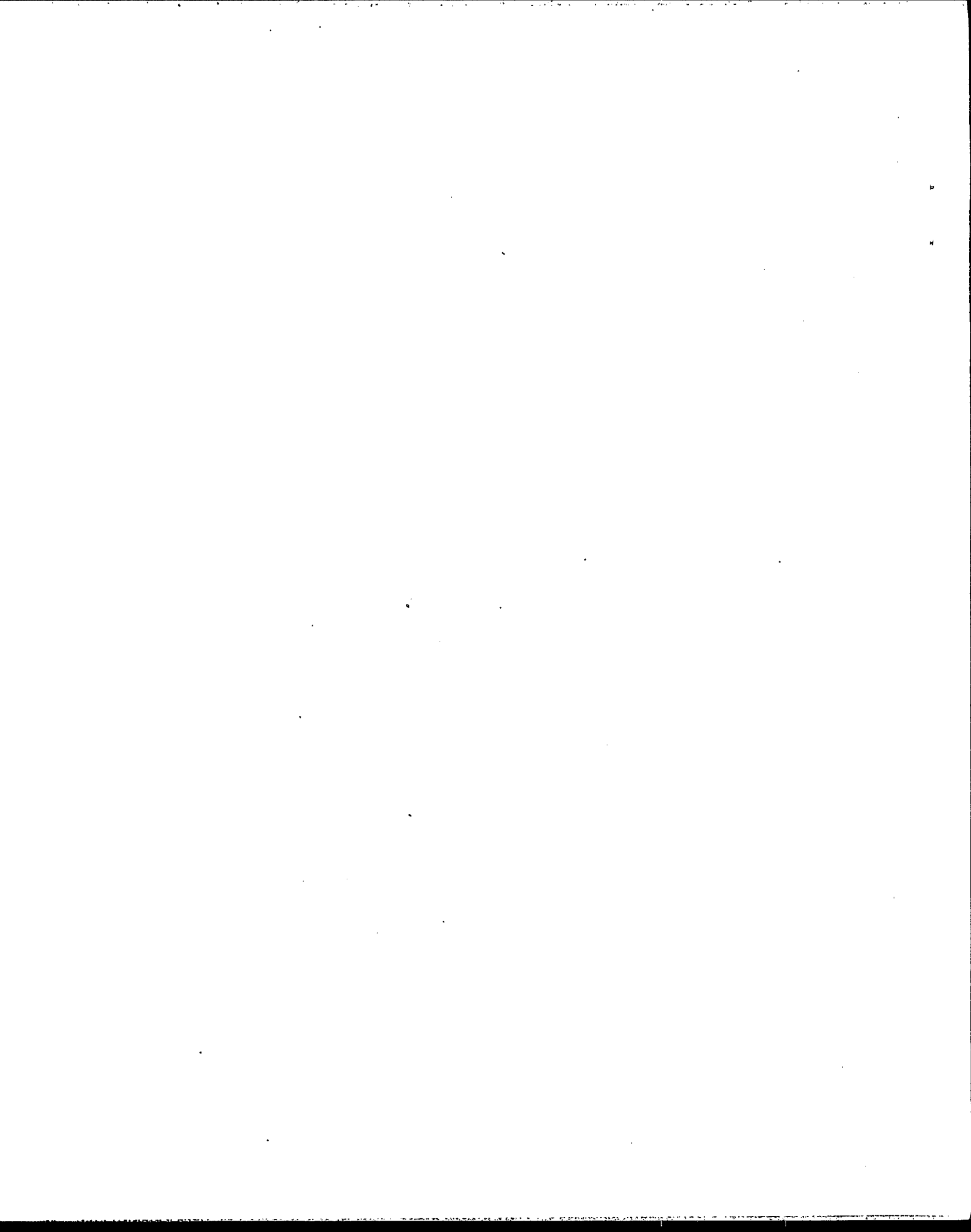
GUIDANCE MANUAL  
FOR  
LEATHER TANNING AND FINISHING  
PRETREATMENT STANDARDS

September 1986

Prepared by:

Industrial Technology Division  
Office of Water Regulations and Standards  
and  
Permits Division  
Office of Water Enforcement and Permits

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401 M Street, S.W.  
Washington, DC 20460





UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

OFFICE OF  
WATER

MEMORANDUM

SUBJECT: Guidance Manual for Leather Tanning and Finishing  
Pretreatment Standards

FROM: Martha G. Prothro, Director  
Permits Division (EN-336)

*Martha Prothro*

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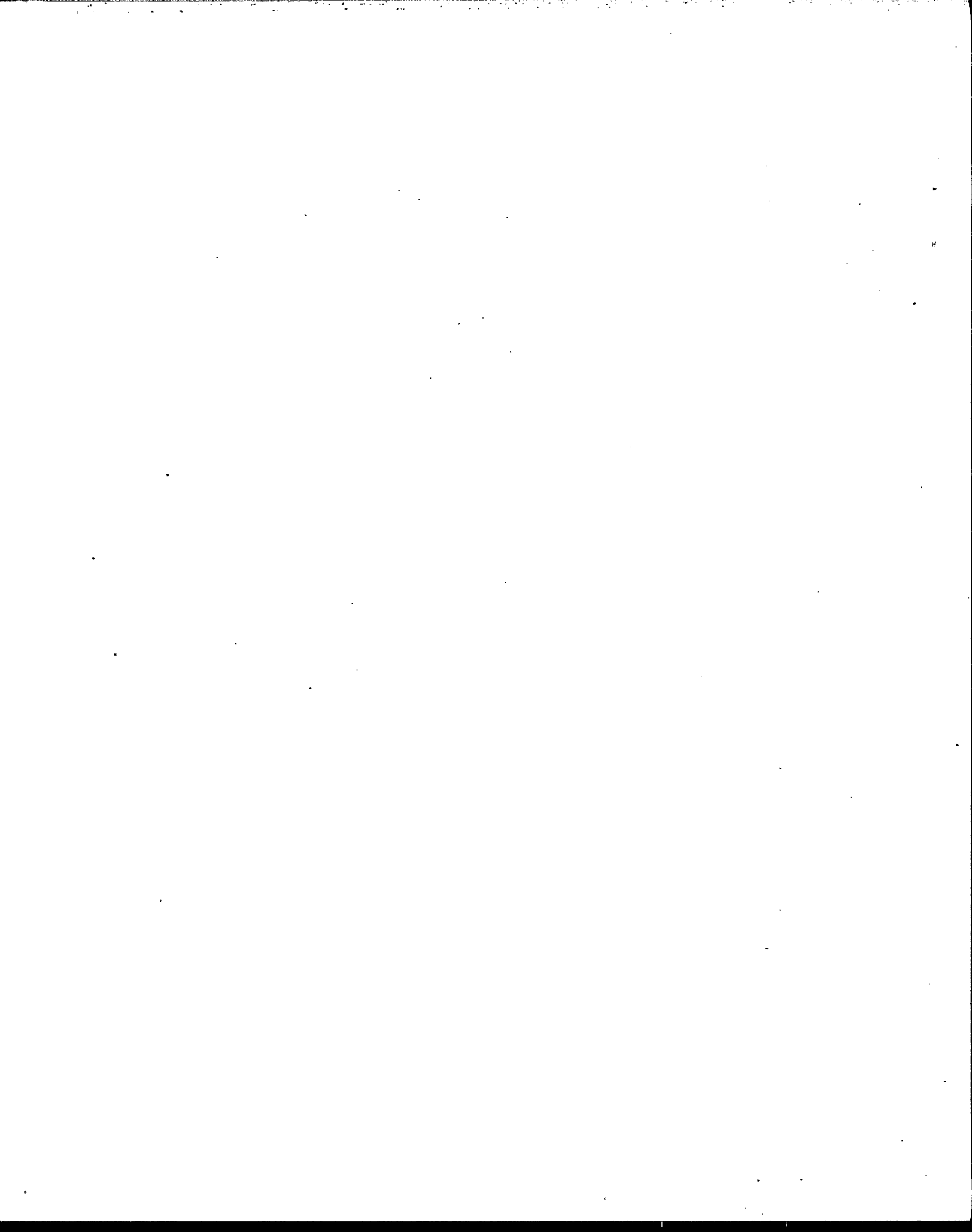
TO: Users of the Guidance Manual

This manual provides information to assist Control Authorities and Approval Authorities in implementing the National Categorical Pretreatment Standards for the Leather Tanning and Finishing Point Source Category (40 CFR Part 425). It is designed to supplement the more detailed documents listed as references in the manual; it is not designed to replace them. If you need more complete information on a specific item, you should refer to the appropriate reference.

EPA developed this manual to fill several needs. First, it should be useful to Control Authorities in responding to most routine inquiries from regulated facilities. More complex inquiries may require the use of the listed references.

Second, the manual addresses application of the combined wastestream formula to integrated facilities with regulated and unregulated wastestreams. It also provides current information on removal credits, variances and reporting requirements. It further incorporates the proposed amendment to the categorical standards reflecting the settlement of litigation issues for the final rule.

This manual is one of a series of industry-specific and program-specific guidance manuals for implementing the pretreatment program (see references). Please feel free to write to either the Office of Water Regulations and Standards (WH-552) or the Office of Water Enforcement and Permits (EN-336) with suggestions, additions or improvements.

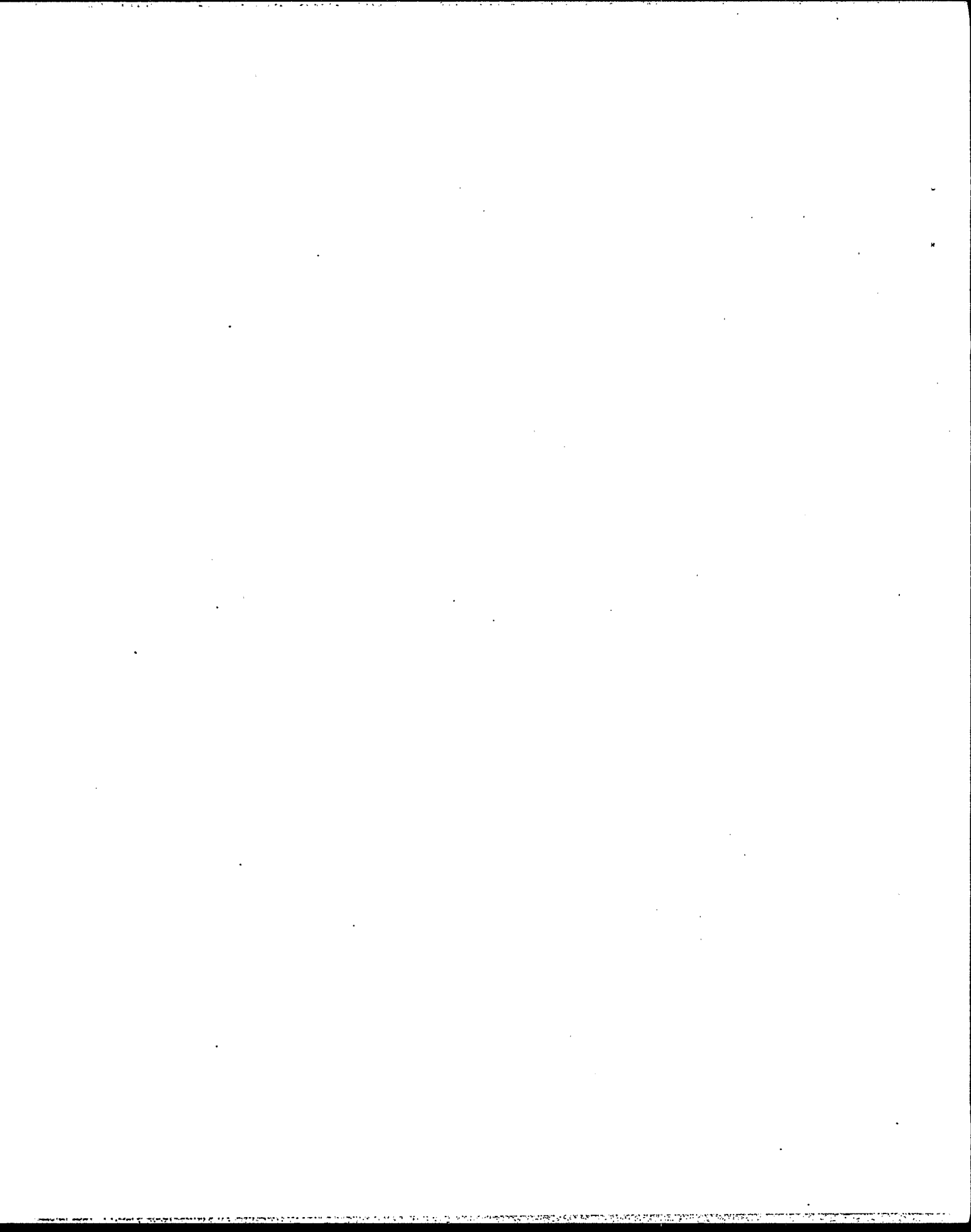


### ACKNOWLEDGEMENTS

We wish to acknowledge the considerable efforts and cooperation of the many people whose contributions helped in the successful completion of this document.

This document was prepared under the direction of Mr. Marvin Rubin, Chief, Analysis and Support Branch, Industrial Technology Division and Dr. James Gallup, Chief, Municipal Programs Branch. Mr. Donald Anderson and Mr. Rex Gile of the Industrial Technology Division and Mr. Timothy Dwyer of the National Pretreatment Program are to be acknowledged for their valuable input. In addition, members of the Office of General Counsel are acknowledged for their important contributions.

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## 1. INTRODUCTION

The National Pretreatment Program establishes an overall strategy for controlling the introduction of nondomestic wastes to publicly owned treatment works (POTWs) in accordance with the overall objectives of the Clean Water Act. Sections 307 (b) and (c) of the Act authorize the Environmental Protection Agency to develop national pretreatment standards for new and existing dischargers to POTWs. The Act made these pretreatment standards enforceable against dischargers to publicly owned treatment works.

The General Pretreatment Regulations (40 CFR Part 403) establish administrative mechanisms requiring nearly 1,500 POTWs to develop local pretreatment programs to enforce Categorical Pretreatment Standards. These Categorical Pretreatment Standards establish specific numerical limitations based on an evaluation of available technologies for particular industrial categories. The numerical limitations are imposed upon pollutants which may interfere with, pass through or otherwise be incompatible with POTWs. As a result of a settlement agreement, the EPA was required to consider development of Categorical Pretreatment Standards for 34 industrial categories with a primary emphasis on 65 classes of toxic pollutants.

This manual will provide guidance to POTWs on the implementation and enforcement of the Categorical Pretreatment Standards for the Leather Tanning and Finishing Category. This document has been prepared using primarily three sources: Federal Register notices for the Leather Tanning and Finishing regulations, the Final Development Document for Leather Tanning and Finishing regulations, which provide technical support for the regulations, and the Settlement Agreement between the Tanners' Council of America, Inc. and EPA, dated December 11, 1984. Portions of this document which reflect changes agreed to in the Settlement Agreement are noted for identification to the reader. These changes must go through the standard public proposal and promulgation rulemaking process to be incorporated into the categorical standards. Proposed amendments incorporating the changes as a result of this Settlement Agreement are scheduled for publication in the Federal Register in the early part of 1986. Additional information on the regulations, manufacturing processes, and control technologies can be found in these sources.

A listing of the references used in the development of this manual is provided at the end of this document.

#### 1.1 HISTORY OF THE LEATHER TANNING AND FINISHING CATEGORICAL PRETREATMENT STANDARDS

Pretreatment standards for the leather tanning and finishing category were first established in 1974 for new sources (40 CFR Part 425, Subparts A-F, 39 FR 12958), and in 1977 for existing sources (40 CFR Part 425, Subparts A-G, 42 FR 15696). In 1979 (44 FR 38746), EPA proposed revisions to Pretreatment Standards for Existing Sources (PSES) and Pretreatment Standards for New Sources (PSNS). On June 6, 1982, EPA published a notice of availability in the Federal Register which made available for public review and comment supplementary technical and economic information and data received after proposal of the regulations (47 FR 23958). The Agency also summarized the preliminary findings of how these supplementary record materials might influence final rulemaking. On November 23, 1982 (47 FR 52848), the regulations were promulgated. The Tanners' Council of America (TCA) challenged the final regulations. On December 11, 1984, a Settlement Agreement between TCA and EPA resolving issues from the challenge of the final rule was executed.

The leather tanning and finishing industry currently includes 158 facilities operating within 9 subcategories. Of the 158 facilities located in the United States, approximately 141 discharge into POTWs. Generally, the tanneries are small family operations, although several are divisions of larger corporations. Approximately 30 percent of the facilities employ less than 50 people, and generate wastewater volumes of less than 100,000 gallons per day. In addition, approximately 50 percent of the facilities are housed in structures over 50 years old. Since the mid 1960's, the industry has experienced a decline in production and profit and continually faces international competition for its consumer markets.

2. LEATHER TANNING AND FINISHING CATEGORICAL  
PRETREATMENT STANDARDS  
(40 CFR 425)

2.1 AFFECTED INDUSTRY

Leather tanning or finishing is the conversion of animal hides or skins into leather. Cattlehides, sheepskins, and pigskins are the major hides and skins used most often to manufacture leather. To a lesser extent, hides and skins of horses, goats, deer, elk, calves, and other animals are also tanned. Cattlehide or cattle-like hide have short hair and are relatively heavy. Deerskin, horsehide, cow bellies, splits (flesh side of tanned hides which is usually processed separately into suede types of leather) and hides of a similar nature are included in this group. Sheep or sheep-like skins have long hair and are relatively light. Goatskin and other similar hides are included in this group. Pig or pig-like skins have short hair or are hairless and are relatively light. This group includes skins which have little hair, yet typically require unhairing operations. The type of raw material (hides or skins) and the amount of processing already performed on the raw materials received by the facility determines the type of processes necessary to produce finished or partially processed leather. Facilities covered by the Leather Tanning and Finishing regulations are included in SIC 3111.

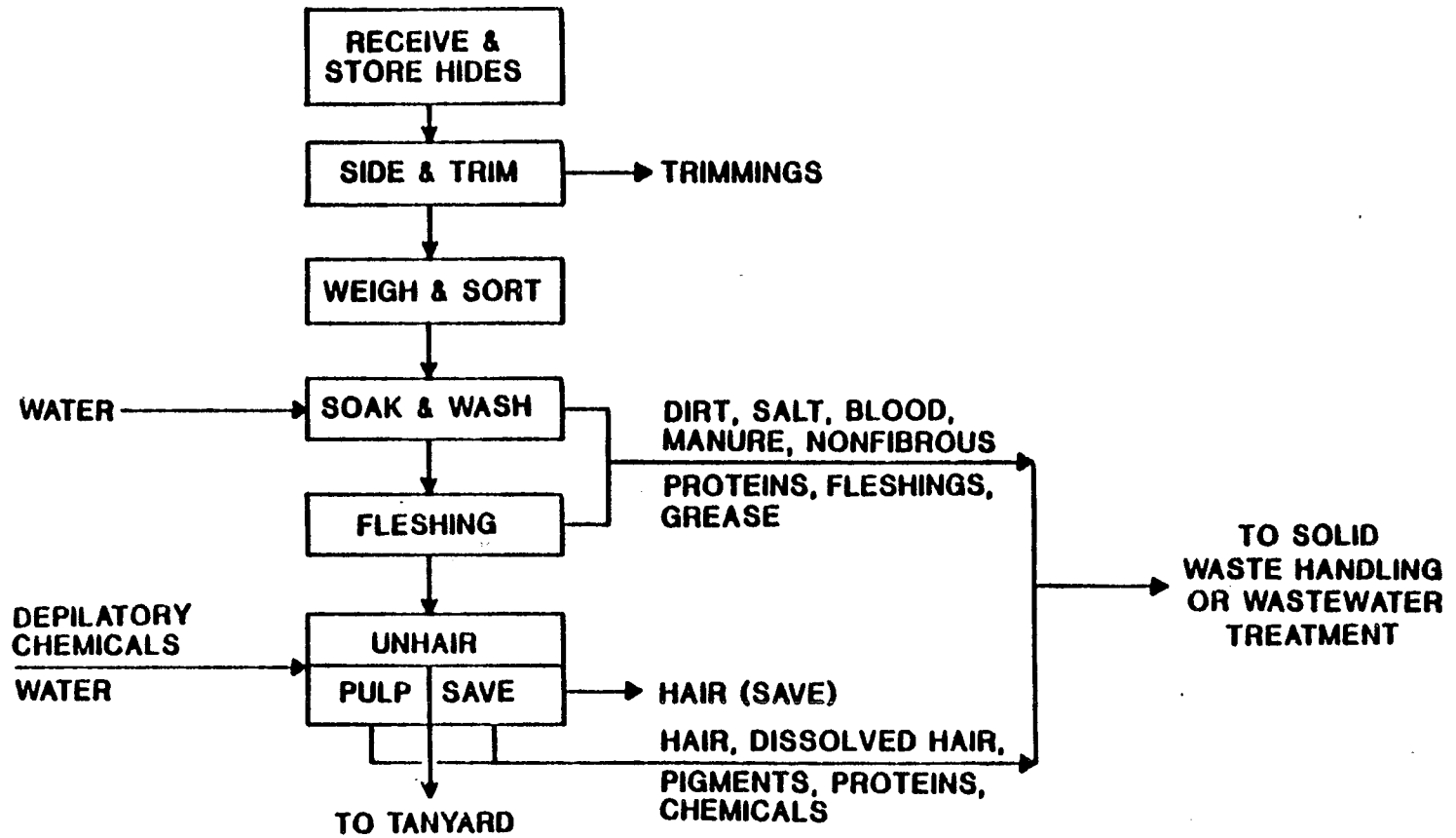
2.2 PROCESS OPERATIONS

It is the inner layer of an animal skin, which consists primarily of the protein collagen, that is made into leather. Tanning is the reaction of the collagen fibers with tannins, chromium, alum, or other tanning agents to help stabilize or preserve the skin to make it useful. There are three major groups of subprocesses required to make finished leather: Beamhouse operations; tanyard processes; and retanning and finishing processes. These processes and types of wastewater generated are described below:

1. Beamhouse operations (summarized in Figure 2.1) consist of four typical subprocesses: Side and trim; soak and wash; fleshing; and unhairing. Side and trim is the cutting of the hide into two sides and trimming of areas which do not produce good leather. In soak and wash processes, the hides or sides are soaked in water for eight to twenty hours to restore the moisture that was lost during curing. Washing removes dirt, salt, blood, manure, and nonfibrous proteins.

FIGURE 2.1

### LEATHER TANNING AND FINISHING INDUSTRY BEAMHOUSE OPERATION



Fleshing is a mechanical operation which removes excess flesh, fat, and muscle from the interior of the hides. Cold water is used to keep the fat congealed. The removed matter is normally recovered and sold for conversion to glue. Unhairing involves using calcium hydroxide, sodium sulfhydrate, and sodium sulfide to destroy the hair (hair pulp) or remove hair roots (hair save), loosen the epidermis, and remove certain soluble skin proteins. A mechanical unhairing machine is used to remove hair loosened by chemicals in the hair save process.

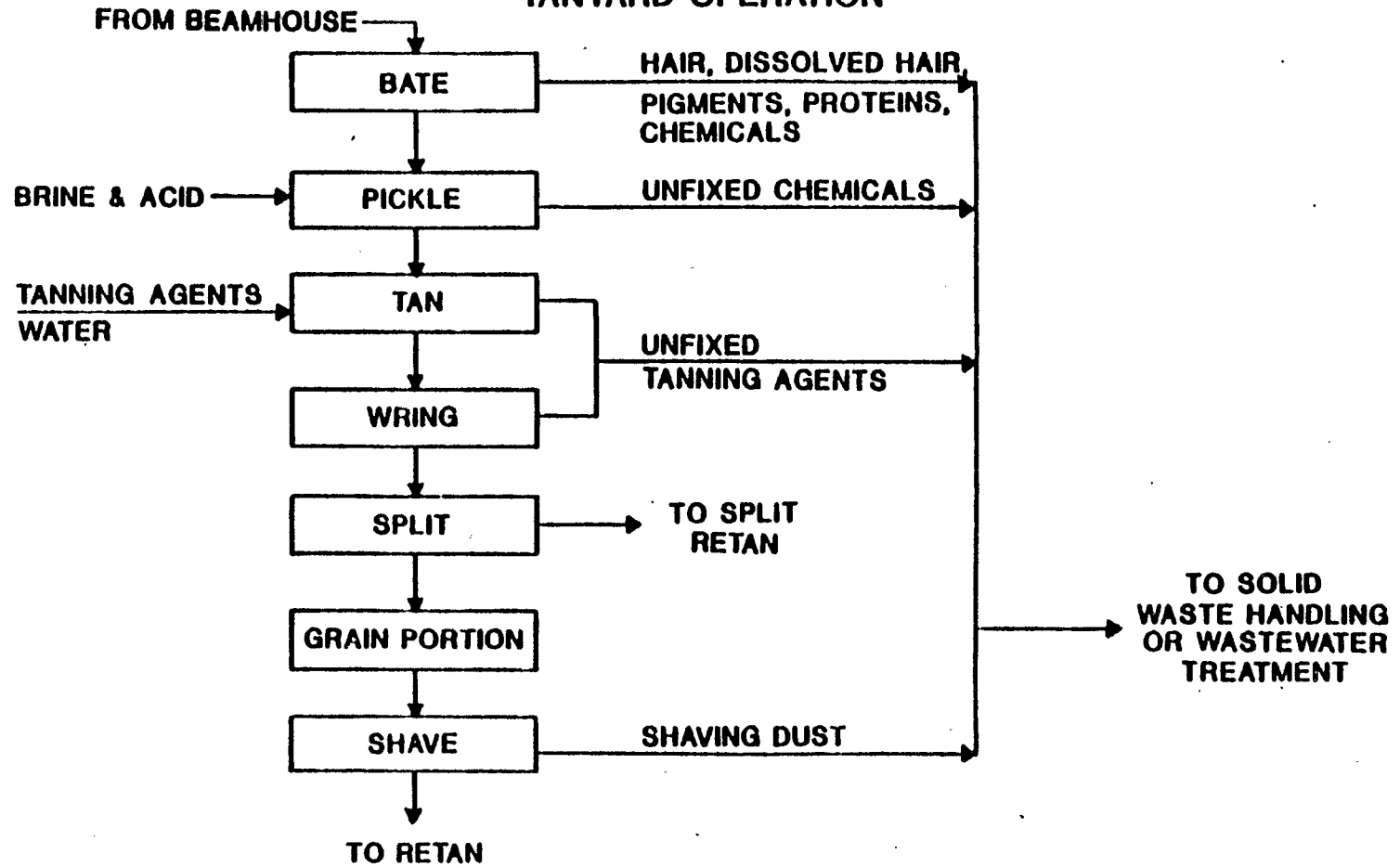
Beamhouse processes typically generate approximately 40 percent of the wastewater volume and approximately 60 percent of the pollutant load (except chromium) from a complete tannery. Washing and soaking produce large quantities of wastewater containing dirt, salt, manure, and other materials. Solvent degreasing, usually performed only on sheepskins and pigskins, generates animal fat and waste skin material, spent detergents, and solvents. Unhairing is performed in an alkaline medium. The hair from the hair save method is usually disposed of in a landfill; however, the hair pulp process completely dissolves the hair. This process is the most significant source of proteinaceous organic and inorganic (lime) pollutants characterized by a high pH (10-12), and substantial amounts of BOD, TSS, sulfides, alkalinity, and nitrogen.

2. Tanyard processes (shown schematically in Figure 2.2) follow the beamhouse operations and consist of bating, pickling, tanning, wringing, splitting, and shaving. Bating involves the addition of salts of ammonium sulfate or ammonium chloride used to convert the residual alkaline chemicals present from the unhairing process into soluble compounds which can be washed from the hides or skins. The addition of bates, enzymes similar to those found in the digestive systems of animals, facilitate the separation of the collagen protein fibers and destroy most of the remaining undesirable constituents of the hide, such as hair roots and pigments. Pickling prepares the hides to accept the tanning agents (i.e., chrome) usually by adding sulfuric acid to provide the acid environment necessary for chromium tanning. In the tanning process, tanning agents such as trivalent chromium, vegetable tannins, alum, syntans, formaldehyde, gluteraldehyde, and heavy oils, convert the raw collagen fibers of the hide into a stable product no longer susceptible to putrefaction or decomposition. They also improve the dimensional stability, resistance to heat, chemicals and abrasion, and flexibility of the raw materials. Vegetable tanning is used in the production of heavy leathers such as sole leather and saddle leather. Chromium tanning is usually preferred by the majority of leather users, i.e., shoe and garment manufacturers. Blue hides (hides after beamhouse and tanyard operations) are wrung to remove excess moisture through a machine similar to a clothes wringer. Splitting adjusts the thickness of the tanned hide to the requirements of the finished product and produces a split ("drop") from the flesh side of the hide. These splits may or may not be retanned and wet finished at the same facility. Shaving removes any remaining fleshy matter from the flesh portion of the hide.



FIGURE 2.2

### LEATHER TANNING AND FINISHING INDUSTRY TANYARD OPERATION



Wastewater from tanyard operations contain inorganic chemical salts, small amounts of proteinaceous hair and waste, and large amounts of ammonia from the bating process. Pickling generates a highly acidic waste (pH of 2.5-3.5) which contains salt. Spent chromium liquors contain high concentrations of trivalent chromium in acid solution with low concentrations of BOD and TSS and elevated temperatures. Discharges (blowdown) from vegetable tanning vats necessary to maintain vegetable tanning liquor quality is highly colored and contains significant amounts of BOD, COD, and dissolved solids.

3. Retanning and wet finishing processes (diagrammed in Figure 2.3) give the tanned hide special or desired characteristics. The steps used include retanning, bleaching, coloring, fatliquoring, and finishing. Retanning is used to give the leather certain special characteristics (different degrees of flexibility) which are lacking after the initial tanning step. The most common retanning agents are chromium, vegetable extracts (used to minimize variation between different parts of the chromium tanned hide), and syntans (used for softer side leathers and in making white or pastel leathers). In the sole leather industry, sodium bicarbonate and sulfuric acid are used to bleach the leather after tanning. Coloring involves combining dyes (usually aniline based) with the tanned skin fibers to form an insoluble compound. Dyes are added in the retanning wheels. Animal or vegetable fatliquors are added to replace the natural oils lost in the beamhouse and tanyard processes. Finishing includes all operations performed on the hide after fatliquoring, and includes finishing to enhance color and resistance to stains and abrasions, smoothing and stretching the skin, drying, conditioning, staking, dry milling, buffing, and plating.

These processes generate wastes with additional quantities of trivalent chromium, tannins, sulfonated oils, and spent dyes, which are low in BOD and TSS, high in COD, and at elevated temperature.

In general, most tanneries perform the entire tanning process, from beamhouse to wet finishing operations. A smaller number perform only beamhouse and tanyard operations and sell their unfinished product (wet "blue" stock) to other tanneries to produce specific leathers.

### 2.3 SUBCATEGORIZATION

Nine subcategories (Table 2.1) have been identified based on distinct combinations of raw materials and leather processing operations. Table 2.2 summarizes the raw materials and processes used by the subcategories, which are described in detail below:

1. Hair Pulp/Chrome Tan/Retan-Wet Finish - facilities which primarily process raw or cured cattle or cattle-like hides into finished

FIGURE 2.3

## LEATHER TANNING AND FINISHING INDUSTRY RETAN-WET FINISH OPERATION

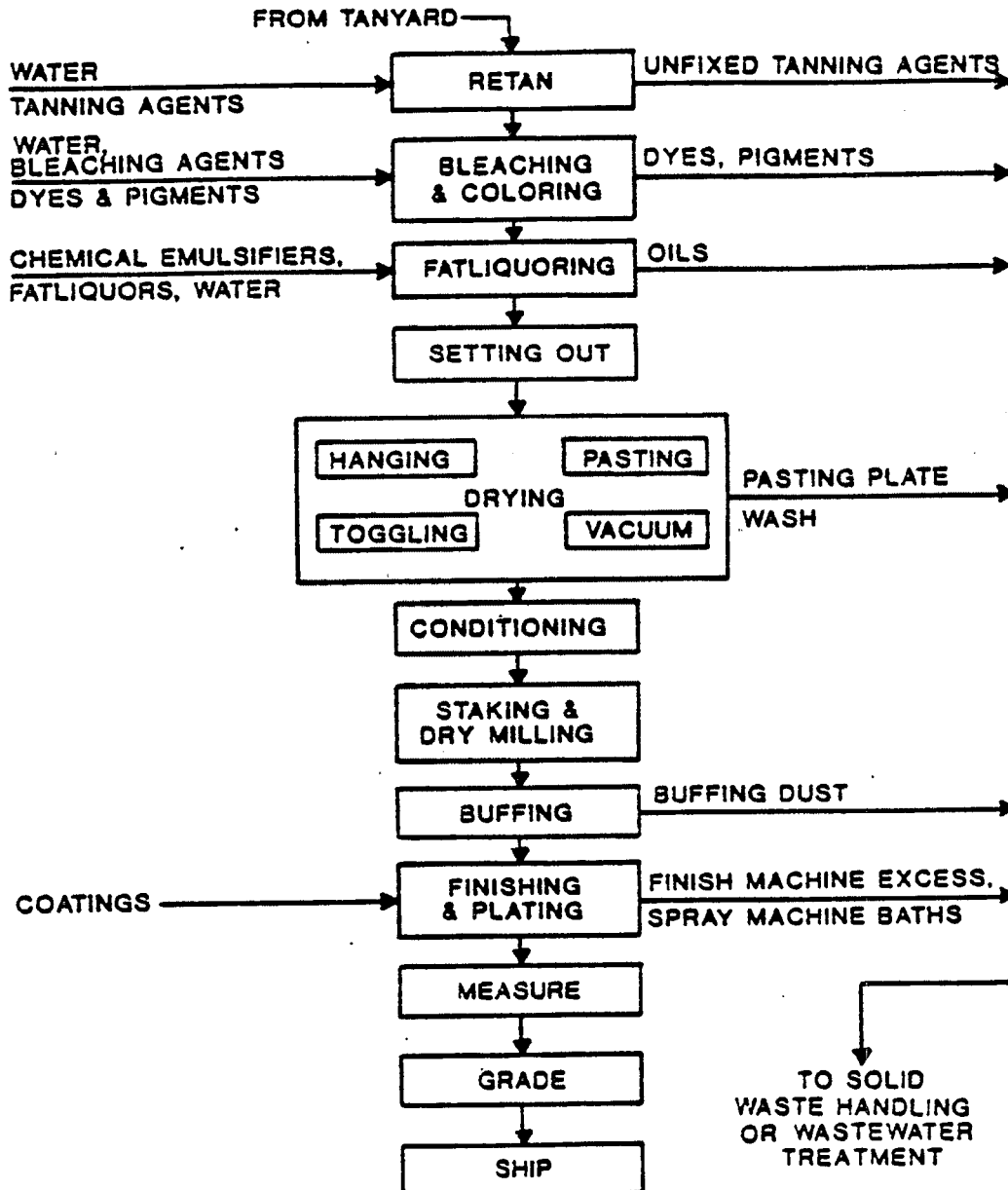


TABLE 2.1

LEATHER TANNING AND FINISHING INDUSTRY  
SUBCATEGORIES

<u>Subcategory</u>	<u>Title</u>
1	Hair Pulp, Chrome Tan, Retan-Wet Finish
2	Hair Save, Chrome Tan, Retan-Wet Finish
3	Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish
4	Retan-Wet Finish (Sides)
5	No Beamhouse
6	Through-The-Blue
7	Shearling
8	Pigskin
9	Retan-Wet Finish (Splits)

TABLE 2.2

## SUBCATEGORY RAW MATERIALS AND PROCESSES

<u>Subcategory</u>	<u>Raw Materials</u>	<u>Major Tanning and Finishing Steps</u>		
		<u>Beamhouse</u>	<u>Tanyard</u>	<u>Retan-Wet Finish</u>
1	Cattlehide Deer, Elk, Moose	Hair Pulp	Chrome Tan	Yes
2	Cattlehide Calfskin	Hair Save	Chrome Tan	Yes
3	Cattlehide Calfskin	Hair Save or Pulp	Non-Chrome Tan	Yes
4	Blue Sides (cattlehide, pigskins)	--	--	Yes
5	Unhaired and Pickled Cattlehides, Sheepskins, Goatskins	--	Chrome or Non-Chrome Tan	Yes
6	Cattlehide	Hair Pulp	Chrome Tan	No
7	Shearlings (wool-on)	--	Chrome or Non-Chrome Tan	Yes
8	Pigskins	Hair Pulp	Chrome or Non-Chrome Tan	Yes
9	Blue Splits (drops) (cattlehide)	--	--	Yes

leather by chemically dissolving the hair (hair pulp), tanning with trivalent chromium, and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, garments, upholstery, gloves, and lining material.

2. Hair Save/Chrome Tan/Retan-Wet Finish - facilities which primarily process raw or cured cattle or cattle-like hides into finished leather by chemically loosening and mechanically removing the hair (hair save), tanning with trivalent chromium, and retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers, handbags, garments, and gloves.
3. Hair Save or Pulp/Non-chrome Retan/Retan-Wet Finish - facilities which process raw or cured cattle or cattle-like hides into finished leather by chemically dissolving (hair pulp), or loosening and mechanically removing the hair (hair save); tanning primarily with vegetable tannins, although other chemicals such as alum, syntans, or oils may be used; and retanning and wet finishing. Primary uses for the final products of this subcategory include sole leather, laces, harnesses, saddle leather, mechanical strap and skirting leather, and sporting good leathers (basketballs, footballs, softballs, baseballs, etc).
4. Retan/Wet Finish (Sides) - facilities which process previously unhaired and tanned "wet blue" grain sides into finished leather through retanning with trivalent chromium, syntans, vegetable tannins, or other tanning agents, coloring with dyes, and wet finishing processes including fatliquoring, drying (especially pasting frame or vacuum), and mechanical conditioning. Primary uses for the final products of this subcategory include shoe uppers, garments, and personal goods.
5. No Beamhouse - facilities which process previously unhaired and pickled cattleskins, sheepskins, or pigskins into finished leather by tanning with trivalent chromium or other agents, then retanning and wet finishing. Primary uses for the final products of this subcategory include garments, shoe uppers, gloves, and lining material.
6. Through-the-Blue - facilities which process raw or cured cattle or cattle-like hides only through the "wet-blue" tanned state by chemically dissolving or loosening the hair and tanning with trivalent chromium. No retanning or wet finishing is performed. The "wet blue" stock produced by this subcategory is subjected to further processing by plants in Subcategory 4 (grain sides) and plants in Subcategory 9 (splits).
7. Shearling - facilities which process raw or cured sheep or sheep-like skins with hair intact into finished leather by tanning with trivalent chromium or other agents, retanning, and wet finishing. Primary uses for hair on sheepskins (shearling) include hospital products, wool lined suede coats and similar garments, or specialty footwear, and seat covers.

8. Pigskin - facilities which process raw or cured pigskins into finished leather by chemically dissolving the hair and tanning with trivalent chromium, then retanning and wet finishing. Primary uses for the final products of this subcategory include shoe uppers and gloves.
9. Retan/Wet Finish (Splits) - facilities which process previously unhaired and tanned splits into finished leather through retanning and wet finishing processes that include coloring, fatliquoring, and mechanical conditioning. Primary uses for the final products of this subcategory include sueded leathers for garments, shoe uppers, and other specialty or personal goods.

#### 2.4 EXCEPTIONS FROM REGULATION

Operations which involve the manufacture of leather goods from finished leather and which are exempt from coverage under the Leather Tanning and Finishing Standards include: facilities in SIC 3131-3149, Shoe and Related Footwear; and SIC 3151-3199, Gloves, Luggage, Personal Goods, and Miscellaneous.

PSES regulations for chromium do not apply to small plants that process less than 275 hides/day in Subcategory 1, less than 350 hides/day in Subcategory 3, and less than 3,600 splits/day in Subcategory 9, because of the potentially disproportionate economic impact on these relatively small facilities. However, small plants in Subcategories 1 and 3 would still be subject to sulfide pretreatment standards and small plants in all subcategories would still be required to comply with the General Pretreatment Regulations (40 CFR 403) including general and specific prohibitions and local limits developed by the POTW Control Authority.

#### 2.5 PRETREATMENT STANDARDS FOR THE LEATHER TANNING AND FINISHING CATEGORY

The pretreatment standards for new and existing sources are analagous to BAT in that they control total chromium and apply to two groups of subcategories, those with unhairing operations (Subcategories 1, 2, 3, 6, and 8), and those without unhairing operations (Subcategories 4, 5, 7, and 9). Pretreatment standards for both existing and new facilities (PSES and PSNS) with unhairing operations include concentration based standards for sulfide and total chromium. Sulfides are controlled because of the potential for interference resulting from the release of massive quantities of hydrogen

sulfide gas in sewers, headworks, and sludge management facilities at POTWs. PSES and PSNS for facilities without unhairing operations include only total chromium concentration based standards. Alternate production based standards based on kilogram per thousand kilograms of raw material are available for new and existing sources, and may be used by the POTW. These alternate production limits are based upon the concentrations specified in the standards and the median water use ratios for existing sources and reduced water use ratios for new sources contained in the settlement agreement. The pretreatment standards for new and existing sources are shown in Table 2.3 and the suggested alternate production based standards are presented in Table 2.4. The monthly average limits are based upon eight days of sampling (approximately twice per week) during any calendar month.

## 2.6 POLLUTANTS EXCLUDED FROM REGULATION

Of the 126 toxic pollutants authorized for regulatory consideration, EPA has excluded 125 pollutants for the leather tanning and finishing industry. Of these pollutants, 71 were not detected by approved 40 CFR Part 136 analytical methods or other state-of-the-art methods and 54 were excluded because there is no economically achievable pretreatment technology available for this industry that will remove these pollutants prior to discharge to POTWs.

## 2.7 COMPLIANCE DATES

The Leather Tanning and Finishing compliance dates are as follows:

Pretreatment Standards for Existing Sources (PSES)	November 25, 1985
Pretreatment Standards for New Sources (PSNS)	On commencement of discharge
Sulfide Pretreatment Standards for Existing Sources	See Section 2.8.3

## 2.8 SULFIDE EXEMPTION

A POTW receiving unhairing wastewaters from tanneries may certify to EPA that the sulfide pretreatment standard applicable to a new or existing source



TABLE 2.3

CONCENTRATION BASED  
PRETREATMENT STANDARDS (PSES AND PSNS)  
FOR LEATHER TANNING AND FINISHING

Subcategory 1\*: Hair Pulp, Chrome Tan, Retan-Wet Finish  
 Subcategory 2 : Hair Save, Chrome Tan, Retan-Wet Finish  
 Subcategory 3\*: Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish  
 Subcategory 6 : Through-The-Blue  
 Subcategory 8 : Pigskin

<u>Pollutant</u>	<u>Daily Maximum (mg/l)</u>	<u>Maximum Monthly Average (mg/l)</u>
Sulfide	24	--
Total Chromium	12	8
pH	between 7.0 and 10.0 (except for Subcategory 3 which is not less than 7)***	

Subcategory 4 : Retan-Wet Finish (sides)  
 Subcategory 5 : No Beamhouse  
 Subcategory 7 : Shearling  
 Subcategory 9\*: Retan-Wet Finish (splits)

<u>Pollutant</u>	<u>Daily Maximum (mg/l)</u>	<u>Maximum Monthly Average (mg/l)</u>
Total Chromium	19	12
pH	between 6.0 and 10.0	

\*The promulgated regulation exempts small tanneries from the chromium pretreatment standards only (PSES and PSNS) as follows:

Subcategory 1: processes less than 275 hides/day\*\*  
 Subcategory 3: processes less than 350 hides/day\*\*  
 Subcategory 9: processes less than 3600 splits/day\*\*

\*\* Small plant specifications in the regulations added in a correction notice (see the Federal Register for June 30, 1983, 48 FR 30115), including annual weight basis and number of working days underlying the daily hide and split limits, will be deleted. Based upon the Settlement Agreement the production basis will be process of hides or splits as shown.

\*\*\*This change to Subcategory 3 pH limitation is a result of the Settlement Agreement.

TABLE 2.4

ALTERNATE PRODUCTION-BASED EFFLUENT LIMITATIONS  
FOR EXISTING SOURCES (PSES)\*  
(kg/kkg of raw material)

Subcategory 1: Hair Pulp, Chrome Tan, Retan-Wet Finish

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.54	0.36
Sulfide	1.08	--

Total chromium standards do not apply to plants processing less than 275 hides/day.

Subcategory 2: Hair Save, Chrome Tan, Retan-Wet Finish

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.50	0.33
Sulfide	1.00	--

Subcategory 3: Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.45	0.30
Sulfide	0.90	--

Total chromium standards do not apply to plants processing less than 350 hides/day.

Subcategory 4: Retan-Wet Finish (Sides)

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total chromium	0.76	0.48

Subcategory 5: No Beamhouse

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.63	0.40

\*The limits have been revised to reflect the median water use ratios for existing sources contained in the settlement agreement.

TABLE 2.4 (continued)

ALTERNATE PRODUCTION-BASED EFFLUENT LIMITATIONS  
FOR EXISTING SOURCES (PSES)\*  
(kg/kg of raw material)

Subcategory 6: Through-The-Blue

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.21	0.14
Sulfide	0.42	--

Subcategory 7: Shearling

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	1.49	0.94

Subcategory 8: Pigskin

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.50	0.33
Sulfide	1.00	--

Subcategory 9: Retan-Wet Finish (Sides)

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.47	0.30

Total chromium standards do not apply to plants processing less than 3,600 splits/day.

\*The limits have been revised to reflect the median water use ratios for existing sources contained in the settlement agreement.

TABLE 2.5

ALTERNATE PRODUCTION-BASED EFFLUENT LIMITATIONS  
FOR NEW SOURCES (PSNS)\*  
(kg/kkg of raw material)

Subcategory 1: Hair Pulp, Chrome Tan, Retan-Wet Finish

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.43	0.29
Sulfide	0.86	--

Total chromium standards do not apply to plants processing less than 275 hides/day.

Subcategory 2: Hair Save, Chrome Tan, Retan-Wet Finish

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.50	0.33
Sulfide	1.00	--

Subcategory 3: Hair Save or Pulp, Non-Chrome Tan, Retan-Wet Finish

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.42	0.28
Sulfide	0.84	--

Total chromium standards do not apply to plants processing less than 350 hides/day.

Subcategory 4: Retan-Wet Finish (Sides)

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total chromium	0.73	0.46

Subcategory 5: No Beamhouse

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.60	0.38

\*The limits have been revised to reflect the reduced water use ratios for new sources contained in the settlement agreement.

TABLE 2.5 (continued)

ALTERNATE PRODUCTION-BASED EFFLUENT LIMITATIONS  
FOR NEW SOURCES (PSNS)\*  
(kg/kg of raw material)

Subcategory 6: Through-The-Blue

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.21	0.14
Sulfide	0.42	--

Subcategory 7: Shearling

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	1.49	0.94

Subcategory 8: Pigskin

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.41	0.27
Sulfide	0.82	--

Subcategory 9: Retan-Wet Finish (Sides)

<u>Pollutant</u>	<u>Daily Maximum</u>	<u>Maximum Monthly Average</u>
Total Chromium	0.40	0.25

Total chromium standards do not apply to plants processing less than 3,600 splits/day.

\*The limits have been revised to reflect the reduced water use ratios for new sources contained in the settlement agreement.

should not apply, provided that the POTW has evaluated the site specific factors that determine the degree of interference attributable to high sulfide concentrations that may present serious hazards to human life.

#### 2.8.1 General Sulfide Criteria

When certifying to the EPA that the sulfide standards should not apply, the POTW must have considered, at the minimum:

1. The presence and characteristics of other industrial wastewater which may increase or decrease sulfide concentrations and/or pH.
2. The characteristics of the sewer/interceptor collection system which either minimize or enhance opportunities for release of hydrogen sulfide gas.
3. The characteristics of the receiving POTWs headworks, preliminary and primary treatment systems, and sludge holding and dewatering facilities which either minimize or enhance opportunities for the release of hydrogen sulfide gas.
4. The occurrence of any prior sulfide related interference.

#### 2.8.2 Specific Sulfide Criteria

The severity of the sulfide problem varies by POTW as a result of the physical characteristics of a POTW's collection system, headworks, and sludge management facilities, and the particular mix and types of industrial and municipal wastewaters. In order to assist POTW's in making the required certification and to aid Regional Offices in reviewing any certifications they may receive, EPA has prepared guidance interpreting the criteria for the sulfide certification set forth in the preamble accompanying the final regulation. Appendix A presents the expanded criteria which were developed by EPA Region V personnel in response to certifications submitted by POTWs with a potential for significant sulfide problems stemming from complex local conditions. This guidance will be very useful in those cases where a POTW receives wastewater from a number of tanning facilities whose wastewater flows constitute a significant percentage of the wastewater received by the POTW. In relatively simple cases, the certifying POTW and the reviewing Regional Office may not need to employ this guidance. The POTW and the Regional Office should make the appropriate decision on whether to employ the guidance on a case-by-case basis.

### 2.8.3 Effective Dates for Sulfide Applicability

The final regulations provided a series of deadlines for POTW's to make findings and notify the public as to their intentions with respect to site specific applications of the sulfide waiver. These deadlines included a requirement that EPA publish a notice in the Federal Register identifying those facilities to which the sulfide pretreatment standards shall not apply.

Several notices have been published by Regional Offices, however, additional provisions to be added to the regulations as a result of the Settlement Agreement will have the effect of altering the application process. These new provisions shall allow a POTW at any time to determine that there have been changed circumstances and to initiate the proceedings and make a determination whether the sulfide standards apply.

The POTW which has granted a waiver can also determine that there have been changed circumstances which justify the application of the standards. In this later case a facility shall comply with the sulfide pretreatment standards no later than 18 months from the date of publication in the Federal Register notice identifying the facility.

### 2.8.4 New Sources

A POTW may certify that the sulfide pretreatment standards do not apply to a new source. This certification must be submitted prior to the commencement of discharge of sulfide and must conform, at a minimum, with the above criteria.

### 2.9 TOTAL CHROMIUM EXEMPTION

The pretreatment standards for chromium are not applicable to plants with mixed subcategory operations if the greatest part of the plant's production is in either subcategory 1, 3 or 9 and if the total plant production is less than the specified number of hides or splits per day for the particular subcategory. The intent of this exemption is to exclude small plants from the chromium pretreatment standards, not to exclude processing operations at medium or large plants.\*

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\* This intent was clarified as part of the Settlement Agreement.

### 3. TREATMENT TECHNOLOGIES

The treatment technologies described in this section are applicable to the control and treatment of wastewaters generated by the leather tanning and finishing industry. The process schematic in Figure 3.1 illustrates the technology basis for the pretreatment limitations. In addition to in-plant controls, the treatment technology consists of screening, catalytic oxidation of sulfides in segregated unhairing wastestreams (applicable to plants in Subcategories 1, 2, 3, 6, and 8, which incorporate sulfide unhairing operations), equalization and coagulation-sedimentation with lime for chromium control of the segregated tanyard and retan-wet finish wastewaters, and neutralization of the combined wastestream. These treatment processes are described in this section.

#### 3.1 IN-PLANT CONTROLS

In-plant controls have often been found to be very cost effective in cleaning up industrial wastewater. In-plant controls applicable to the leather tanning and finishing industry include good housekeeping, stream segregation, water conservation, recycle or reuse of concentrated liquors, and process modifications.

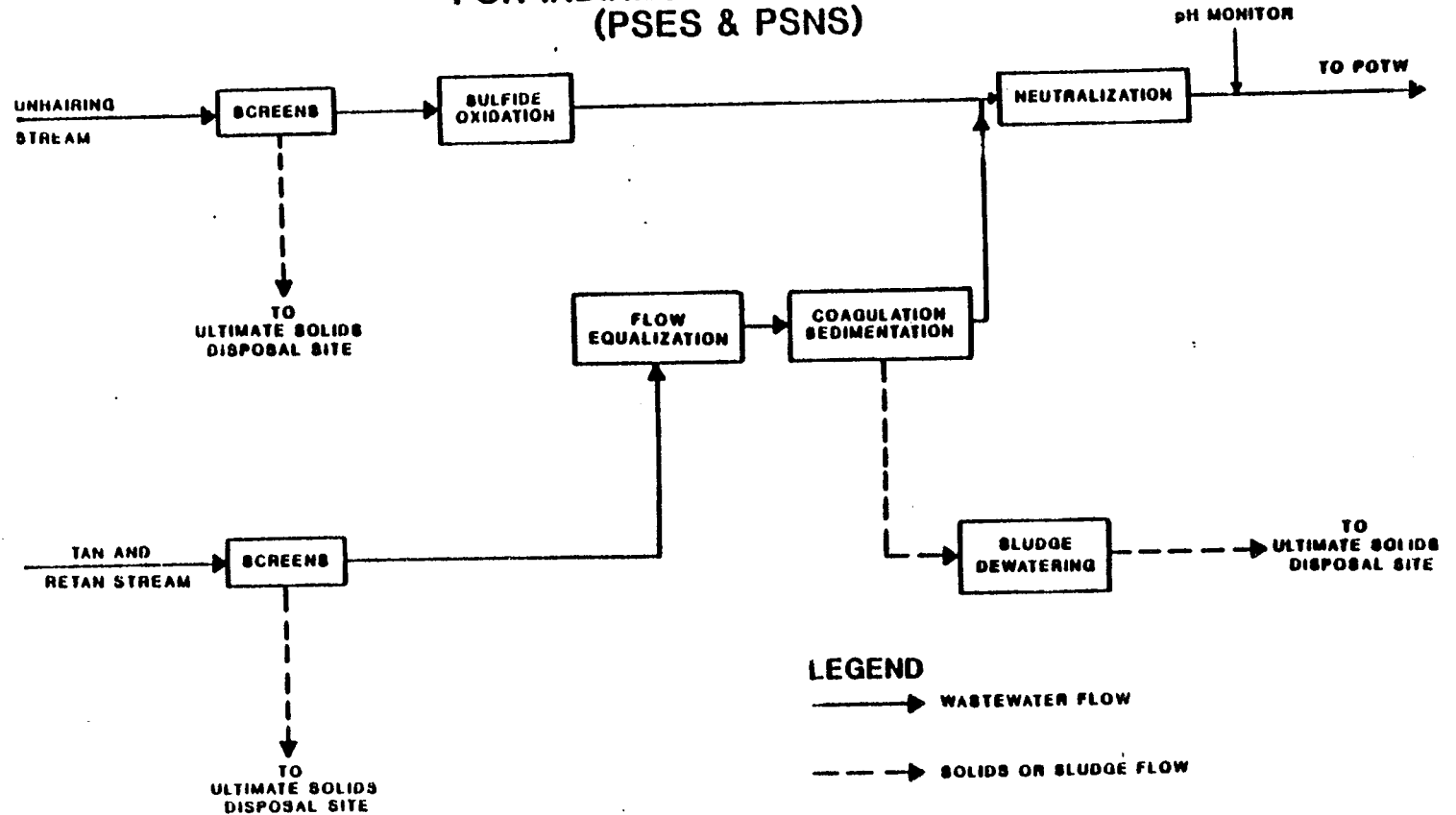
1. Good housekeeping practices include general procedures and management functions to (1) reduce chemical spills resulting from carelessness, (2) prepare a program to control and clean up unavoidable chemical spills, (3) repair or replace faulty equipment, and (4) install automatic monitoring devices to detect abnormal discharges of hazardous gases or polluting substances.

2. Stream segregation is the initial step in implementing many in-plant controls. Because of the difference in wastestream characteristics from beamhouse (high pH and sulfides) and tanning (low pH and chromium) operations, more efficient control can be achieved through the use of a treatment process specifically designed for the related pollutant. Further segregation of spent solvents, concentrated chromium bearing liquors, buffing dust scrubber water, and pickling liquors lead to the reuse or recycling of spent liquors and may decrease the size of the treatment facility for a specific pollutant. In



FIGURE 3.1

### LEATHER TANNING AND FINISHING INDUSTRY PRETREATMENT PROCESS SCHEMATIC FOR INDIRECT DISCHARGERS (PSES & PSNS)



general, wastestream segregation provides the opportunity for lower water use requirements and reduced usage of processing chemicals, thereby reducing the volume and pollutant content of wastewater generated and the cost of treating these wastewaters.

3. Water conservation attempts to reduce water usage in the tannery operations. Batch rinsing employing a closed door rotating tanning drum or using countercurrent washing, has been found to be very efficient. Hide processors provide the opportunity for lower floats and facilitate washing and waste liquor reuse. Dry bag house collection of buffing dust rather than wet scrubbing also eliminates a source of wastewater and very fine suspended solids which can be difficult to treat. Where this is not implemented, the separation of buffing dust scrubber water for treatment and reuse also has been proven to be effective. An additional method of conserving water is recycling cooling water and pasting frame water rather than using once through systems.

4. Reuse of process solutions reduces water use and therefore reduces the discharge of a particular pollutant. The use of highly concentrated depilatory chemicals in the hair removal process provides the opportunity for increased sulfide liquor reuse. The simplest method of sulfide reuse involves screening, storing, and refortifying the spent liquor before reuse. Three methods are generally used to recover chromium from process wastewaters: (1) isolating the spent chromium tanning solutions for reuse in the pickling process; (2) concentrating segregated spent chromium tanning liquors by chemical precipitation for use in formulating new chromium tanning liquors; and (3) incinerating chromium-bearing sludges and recovering hexavalent chromium from the incinerator ash. The recovery of vegetable tannins using the Liritan method substantially reduces the amount of tannins discharged in the wastewater and enables tanners to economize in the purchase of the vegetable tannins. The Liritan process employs intermediate coloring vats which act as barriers to salt carryover from pickling into the tannery liquors.

5. Manufacturing process modifications include alternative hide preservation methods, reduction of lime in unhairing operations, enzyme

unhairing for hair-save operations, in-situ sulfide oxidation, and ammonia substitution. Alternative hide preservation methods are designed to reduce the salt content of hides, and, in turn, wastewaters. These methods are intended to preserve the untanned hides for shorter periods of time. Alternative preservatives include refrigeration; boric acid; combinations of zinc, chlorite, or hypochlorite, and sodium pentachlorophenate; and sulfide combined with acetic acid. Of these, the latter two are the most economical. The reduction of lime reduces the amount of sludge produced and decreases the amount of acid required for pH neutralization. Enzyme unhairing, a method used for removal of hair when the hair will be sold, reduces the total nitrogen content in the unhairing wastes as compared with hair wastes that contain the fully dissolved hair from the hair-pulp method. In-situ sulfide oxidation is performed in the unhairing vessel and converts sulfide to sulfate with manganese (II) ion as a catalyst. It is most often used as an end-of-pipe treatment process and will be described in a later section. Substitution of ammonium sulfate by epsom salts (magnesium sulfate heptahydrate) can be used in deliming to reduce ammonia concentrations. However, loss in the hide weight, non-uniform grain of pickled bellies, and build-up of magnesium salts are sometimes experienced.

### 3.2 TREATMENT PROCESSES FOR SEGREGATED WASTESTREAMS

Treatment processes that apply to the segregated wastestreams from the beamhouse and from the tanyard and retan-wet finish operations are screening, sulfide oxidation, protein precipitation, and reduction and removal of ammonia, as described below.

1. Screening is employed to protect downstream equipment and to remove suspended solids such as hair, buffing dust, and hide and leather scraps from fleshing and hide washing operations. Several types and sizes of screens are often installed, but should include bar screens (already in place at most tanneries) and fine screens (e.g., 0.040 inch openings) which few tanneries have in place. Operated correctly, screening equipment provides for efficient and necessary preliminary wastewater treatment.

2. Sulfide Oxidation in tannery wastes is accomplished most often by catalytic oxidation, chemical oxidation, and precipitation. In catalytic

oxidation of sulfide, the sulfide bearing wastes are collected in a suitable tank, manganese (II) ion is added, and the waste is aerated. Thiosulfate is the primary end product, although sulfite and sulfate also are present. Catalytic oxidation is widely used and has the advantage of reducing the alkalinity of unhairing liquor. Hydrogen peroxide can also be used to oxidize sulfides in tannery wastes. When the pH is reduced to below 8.0, the addition of hydrogen peroxide causes sulfide to be oxidized to sulfur. The disadvantage of this method is the high cost of the chemicals.

Sulfide precipitation by the addition of iron salts minimizes the possibility of oxidized sulfur reverting to sulfide. However, a large quantity of relatively expensive chemicals are required and more solid waste is generated.

3. Flue Gas Carbonation for Protein Precipitation is a method in which carbon dioxide from the tannery's boiler stack gas is used as an inexpensive source of acid to neutralize caustic alkalinity and reduce pH. At the lower pH, protein in the beamhouse wastes flocculate and settle. The sludge generated is rich in lime and protein and may be used as a soil conditioner or protein supplement in animal feed. Removing colloidal proteins also enhances coagulation and sedimentation downstream.

4. Ammonia Reduction by physical means are most effective when applied to concentrated waste, such as the delimiting wastestream. Evaporating water from the waste enables ammonium sulfate to be precipitated and removed. With the addition of phosphoric acid it is possible to precipitate the ammonia as insoluble calcium ammonium sulfate. Ammonium sulfate is also insoluble in a solution of ethanol and water. Additionally, reverse osmosis can be used to concentrate aqueous ammonium sulfate.

### 3.3 END-OF-PIPE TREATMENT PROCESSES

End-of-pipe treatment processes are applied to entire wastestreams and may include flow equalization, sedimentation, coagulation-sedimentation, biological treatment, and filtration.

1. Flow Equalization improves the consistency of other treatment processes' performance by dampening flow surges, diluting slugs of concentrated wastes, partially neutralizing high and low pH waste fractions, and providing a relatively constant rate of flow to downstream treatment processes.

2. Sedimentation is one of the most widely used processes to treat individual and combined wastewater streams. Primary clarification removes suspended solids from tannery wastewater that are sources of BOD, COD, TKN, and certain toxic pollutants, particularly chromium.

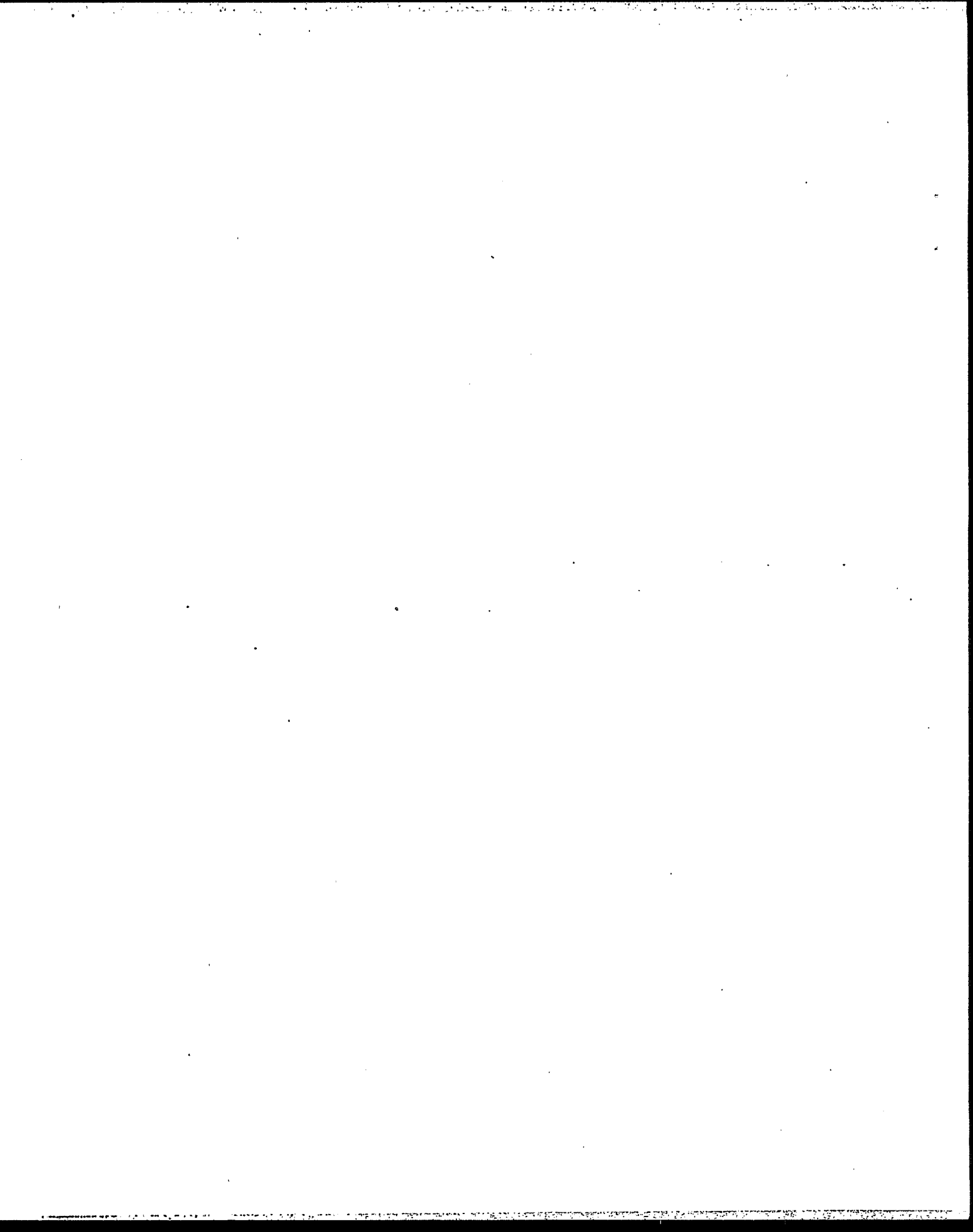
3. Coagulation-Sedimentation - Coagulation with alum, lime, and polymer significantly improves the performance of sedimentation in removing suspended solids, chromium, and other pollutants in the wastestream. When applied to segregated wastestreams, coagulation-sedimentation provides cost-effective pretreatment to achieve PSES and PSNS. In conjunction with other treatment processes, this method has shown to be very effective in removing pollutants.

4. Biological Treatment removes colloidal and dissolved biodegradable organic matter, suspended solids, and some toxic pollutants. Trickling filters, lagoons, activated sludge, and rotating biological contactors (RBCs) are all biological treatment processes that may be employed. The activated sludge process generally is preferred due to its greater consistency in pollutant removal capability, especially its ability to operate more efficiently in cold weather. Upgraded biological treatment incorporates nitrification capabilities and the addition of powdered activated carbon to aeration basins.

5. Filtration in deep bed granular media filters is a physical-chemical process that involves removal of residual suspended solids by different filtered media, such as different grades of sand and anthracite coal. Because of the relationship between suspended solids levels and total chromium, multimedia filtration results in additional removal of chromium.

#### 3.4 SOLIDS HANDLING AND DISPOSAL

Thickening of sludges is designed so that smaller and more efficient equipment may be used in dewatering the sludge. Water removal and the corresponding reduction in weight and volume of the sludge is the main objective of the dewatering process. Common processes for dewatering include vacuum filtration, sludge drying on beds, centrifugation, and pressure filtration. Conditioning is performed to improve dewatering rates, solids capture, and compactability. Stabilization of sludge reduces its putrescible and pathogenic characteristics, thereby reducing the impact to the environment upon disposal.



## 4. REQUIREMENTS OF THE GENERAL PRETREATMENT REGULATIONS

### 4.1 INTRODUCTION

This section provides a brief overview of the General Pretreatment Regulations and identifies those provisions of the Regulations which have a direct bearing on the application and enforcement of Categorical Pretreatment Standards for the Leather Tanning and Finishing category.

The General Pretreatment Regulations for Existing and New Sources (40 CFR Part 403) establish the framework and responsibilities for implementation of the National Pretreatment Program. The effect of 40 CFR Part 403 is essentially three-fold. First, the General Pretreatment Regulations establish general and specific discharge prohibitions as required by Sections 307(b) and (c) of the Clean Water Act. The general and specific prohibitions are described in Section 403.5 of the Pretreatment Regulations and apply to all nondomestic sources introducing pollutants into a POTW whether or not the source is subject to Categorical Pretreatment Standards.

Second, the General Pretreatment Regulations establish an administrative mechanism to ensure that National Pretreatment Standards (Prohibited Discharge Standards and Categorical Pretreatment Standards) are applied and enforced upon industrial users. Approximately 1,500 POTWs are required to develop a locally run pretreatment program to ensure that non-domestic users comply with applicable pretreatment standards and requirements.

Third, and most importantly for the purposes of this guidance manual, the General Pretreatment Regulations contain provisions relating directly to the implementation and enforcement of the Categorical Pretreatment Standards. Reporting requirements, local limits, monitoring or sampling requirements, and category determination provisions are discussed. POTW representatives should refer to 40 CFR Part 403 for specific language and requirements where appropriate.



## 4.2 CATEGORY DETERMINATION REQUEST

An existing industrial user (IU) or its POTW may request written certification from EPA or the delegated State specifying whether or not the industrial user falls within a particular industry category or subcategory and is subject to a categorical pretreatment standard. Although the deadline for submitting a category determination request by existing industrial users subject to the Leather Tanning and Finishing categorical pretreatment standards has passed, a new industrial user or its POTW may request this certification for a category determination anytime prior to commencing its discharge. Section 403.6(a) does not preclude leather tanning and finishing facilities from changing operations which would in turn automatically change their subcategorization status. Facilities that are planning to change their subcategorization status and are unsure which subcategory they will fall into, should request a written category determination from the Agency as to whether the facility falls within a particular subcategory prior to commencing discharges which would fall within that subcategory.\* The contents of a category determination request and procedures for review are presented in Section 403.6(a) of the General Pretreatment Regulations.

## 4.3 MONITORING AND REPORTING REQUIREMENTS OF THE GENERAL PRETREATMENT REGULATIONS

In addition to the requirements contained in the Leather Tanning and Finishing Categorical Pretreatment Standards, industrial users subject to these Standards must fulfill the reporting requirements contained in Section 403.12 of the General Pretreatment Regulations. These requirements include the submission of baseline monitoring reports, compliance schedules, compliance reports (initial and periodic), notices of slug loading, and record-keeping requirements. Each of these reporting requirements is briefly summarized below.

### 4.3.1 Baseline Monitoring Reports

All industrial users subject to Categorical Pretreatment Standards must submit a baseline monitoring report (BMR) to the Control Authority. The purpose of the BMR is to provide information to the Control Authority to

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\*This statement is taken from part of the Settlement Agreement.

document the industrial user's current compliance status with a Categorical Pretreatment Standard. The Control Authority is defined as the POTW if it has an approved pretreatment program, otherwise the BMR will be submitted to the State (if the State has an approved State Pretreatment Program) or to the EPA Region. Additional guidance on BMR reporting is available from the EPA Regional Pretreatment Coordinator.

#### BMR Due Dates

Section 403.12(b) requires that BMRs be submitted to the Control Authority within 180 days after the effective date of a Categorical Pretreatment Standard or 180 days after the final administrative decision made upon a category determination request [403.6(a)(4)], whichever is later. The due date for leather tanning and finishing BMRs was July 5, 1983.

#### BMR Content

A BMR must contain the following information as required by Section 403.12(b).

1. Name and address of the facility, including names of operator(s) and owner(s).
2. List of all environmental control permits held by or for the facility.
3. Brief description of the nature, average production rate and SIC code for each of the operation(s) conducted, including a schematic process diagram which indicates points of discharge from the regulated processes to the POTW.
4. Flow measurement information for regulated process streams discharged to the municipal system. Flow measurements of other wastestreams will be necessary if application of the combined wastestream formula is necessary.
5. Identification of the pretreatment standards applicable to each regulated process and results of measurements of pollutant concentrations and/or mass. All samples must be representative of daily operations and results reported must include values for daily maximum and average concentration (or mass, where required). Where the flow of the regulated stream being sampled is less than or equal to 250,000 gallons per day, the industrial user must take three samples within a two week period. Where the flow of the stream is greater

than 250,000 gallons per day, the industrial user must take six samples within a two week period. If samples cannot be taken immediately downstream from the regulated process and other wastewaters are mixed with the regulated process, the industrial user should measure flows and concentrations of the other wastestreams sufficient to allow use of the combined wastestream formula.

6. Statement of certification concerning compliance or noncompliance with the Pretreatment Standards.
7. If not in compliance, a compliance schedule must be submitted with the BMR that describes the actions the user will take and a timetable for completing those actions to achieve compliance with the standard. This compliance schedule must contain specific increments of progress in the form of dates for the commencement and completion of major events, however, no increment of the schedule shall exceed 9 months. Within 14 days of each completion date in the schedule, the industrial user shall submit a progress report to the Control Authority indicating whether or not it complied with the increment of progress to be met on such date, and, if not, the date on which it expects to comply with this increment of progress and the steps being taken to return to the schedule.

#### 4.3.2 Report on Compliance

Within 90 days after the compliance date for the Leather Tanning and Finishing Pretreatment Standards or in the case of a New Source following commencement of the introduction of wastewater into the POTW, any industrial user subject to the Standards must submit to the Control Authority a "report on compliance" that states whether or not applicable pretreatment standards are being met on a consistent basis. The report must indicate the nature and concentration of all regulated pollutants in the facility's regulated process wastestreams; the average and maximum daily flows of the regulated streams; and a statement of whether compliance is consistently being achieved, and if not, what additional operation and maintenance and/or pretreatment is necessary to achieve compliance. See 40 CFR 403.12(d).

#### 4.3.3 Periodic Reports on Continued Compliance

Unless required more frequently by the Control Authority, all industrial users subject to the Leather Tanning and Finishing Categorical Pretreatment Standards must submit a biannual "periodic compliance report" during the months of June and December. The report shall indicate the precise nature and

concentrations of the regulated pollutants in its discharge to the POTW, the average and maximum daily flow rates of the facility, the methods used by the indirect discharger to sample and analyze the data, and a certification that these methods conformed to those methods outlined in the regulations. See 40 CFR 403.12(e).

#### 4.3.4 Notice of Slug Loading

Section 403.12(f) requires industrial users to notify the POTW immediately of any slug loading of any pollutant, including oxygen demanding pollutants (BOD, etc.) released to the POTW system at a flow rate and/or pollutant concentration which will cause interference with the POTW.

#### 4.3.5 Monitoring and Analysis to Demonstrate Continued Compliance

Section 403.12(g) states that the frequency of monitoring to demonstrate continued compliance shall be prescribed in the applicable Pretreatment Standard. Since Leather Tanning and Finishing Pretreatment Standards do not establish any monitoring frequency, the appropriate Control Authority must establish the monitoring frequency to adequately demonstrate that indirect dischargers subject to these pretreatment standards are in compliance with the applicable standards. Unless otherwise noted in the appropriate paragraph of Section 403.12, the monitoring frequency established by the Control Authority shall be used in the baseline monitoring report (403.12(b)(5)), the report on compliance with categorical pretreatment standard deadline (403.12(d)), and the periodic reports on continued compliance (403.12(e)).

Sampling and analysis shall be in accordance with the procedures established in 40 CFR Part 136 and any amendments to it or shall be approved by EPA. When Part 136 techniques are not available or are inappropriate for any pollutant, then sampling and analysis shall be conducted in accordance with procedures established by the POTW or using any validated procedure. However, all procedures for sampling and analysis not included in Part 136 must be approved by EPA.

An alternative sulfide analytical method was included in the Leather Tanning and Finishing regulation based on a method utilized by the Society of Leather Trades' Chemists (Method SLM 4/2). The sulfide method (iodometric titration) promulgated under Section 304(h) of the Act was subject to interferences, and therefore was not selected as the basis of the regulation. The outline of this SLM 4/2 method can be found in 40 CFR Part 425.03\*, Leather Tanning and Finishing Category regulations, and is contained in Appendix B, Part (b).

One of the issues raised by the industry in litigation of the regulations was that even the SLM 4/2 method, used widely in the industry for chrome tanning process control, was subject to interferences from highly colored (e.g., vegetable tanning) wastewaters. In response to this criticism, the Agency and the industry trade association conducted a cooperative sampling and analytical method development program. As a result of this cooperative program, the industry and EPA agreed that the SLM 4/2 is inappropriate for vegetable tanning facilities. Accordingly, under the Settlement Agreement, EPA will propose an alternative analytical method (the modified Monier-Williams Method) for facilities with vegetable tanning wastewaters. This alternative analytical method [see Appendix B, Part (c)] also may be used for analysis of sulfide in all other wastewaters.

#### 4.3.6 Compliance Monitoring with Multiple Outfalls

In certain cases where an indirect discharging plant does not combine its process wastewaters for treatment and discharges through multiple outfalls, a composite sampling of the multiple outfalls could be accepted. A single composite sample for multiple outfalls must be comprised of representative process wastewaters from each outfall. A composite sample must be combined in proportions determined by the ratio of the process wastewater flow in each outfall to the total flow of process wastewaters discharged through all outfalls. Flow measurement for each outfall must be representative of the plant's operation. An analysis of the total sample would then be compared to

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\*Will be found in Appendix A to 40 CFR Part 425 of the proposed amendments to 40 CFR 425 implementing the settlement agreement.

the applicable categorical standard to determine compliance.\* If nonprocess wastewater is combined with process wastewater or if a plant has operations in more than one subcategory, the plant would have to use the combined wastestream formula to make this calculation.

#### 4.3.7 Signatory Requirements for Industrial User Reports

All reports submitted by industrial users (BMR, Initial Report on Compliance, and Periodic Reports, etc.) must be signed by an authorized representative in accordance with Section 403.12(k).

#### 4.3.8 Recordkeeping Requirements

Any industrial user subject to the reporting requirements of the General Pretreatment Regulations shall maintain records of all information resulting from any monitoring activities required by 403.12 for a minimum of three years [403.12(n)]. These records shall be available for inspection and copying by the Control Authority.

#### 4.4 APPLICATION OF THE COMBINED WASTESTREAM FORMULA

One provision of the General Pretreatment Regulations that will often be used by POTWs and industries to properly monitor and report on compliance with Categorical Pretreatment Standards, is the Combined Wastestream Formula (CWF) [40 CFR 403.6(e)]. The CWF is a mechanism for calculating appropriate limitations specified in regulations applicable to a wastewater in which process wastestreams are mixed with regulated, unregulated or dilution streams, thereby producing a mixed effluent. The CWF is applied to the mixed effluent to account for the presence of the additional wastestreams.

The following definitions and conditions are important to the proper use of the CWF.

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\*This portion of the discussion concerning the multiple outfall requirements results from the Settlement Agreement.

## Definitions

- Regulated Process Wastestream - an industrial process wastestream regulated by National Categorical Pretreatment Standards.
- Unregulated Process Wastestream - an industrial process wastestream that is not regulated by a categorical standards.
- Dilute Wastestream - Boiler blowdown, sanitary wastewater, non-contact cooling water or blowdown, and Paragraph 8 excluded wastestreams containing none of the regulated pollutant or only trace amounts of it.

Note: These definitions apply to individual pollutants. A wastestream from a process may be "regulated" for one pollutant and "unregulated" for another. In addition, the May 17, 1984 amendment to the CWF allows the Control Authority to exercise its discretion to determine whether boiler blowdown and noncontact cooling streams are dilution or unregulated process streams.

- Concentration-Based Limit - a limit based on the relative strength of a pollutant in a wastestream, usually expressed in mg/l (lb/gal).
- Mass-Based Limit - a limitation based on the actual quantity of a pollutant in a wastestream, usually expressed in kg or lb per day.
- Production-Based Limit - a limitation based on the quantity of a pollutant in a wastestream with respect to production levels, usually expressed in kg per 1000 kkg of metal processed.

### 4.4.1 CWF Conditions

To ensure proper application of the CWF, the following conditions must be met by a municipality and its industries [40 CFR 403.6(e)]:

- Alternative discharge limits that are calculated in place of a categorical pretreatment standard must be enforceable as categorical standards.
- Calculation of alternative limits must be established for all regulated pollutants in each of the regulated processes.
- Alternative limits must be established for all regulated pollutants in each of the regulated processes.
- Both daily maximum and long-term average (usually monthly) alternative limits must be calculated for each regulated pollutant.
- Alternative limits must be established for all regulated pollutants in each of the regulated processes.
- If process changes at an industry warrant, the Control Authority may recalculate the alternative limits at its discretion or at

the request of the industrial user. The new alternative limits must be calculated and become effective within 30 days of the process change.

- The Control Authority may impose stricter alternative limits, but may not impose alternative limits that are less stringent than the calculated limits.
- A calculated alternative limit cannot be used if it is below the analytical detection limit, the IU must either: 1) not combine some of the dilute streams before they reach the combined treatment facility, or 2) segregate all wastestreams entirely.

#### 4.4.2. Monitoring Requirements for Industrial User Using the CWF

Requirements for self-monitoring by an industrial user are necessary to ensure compliance with the alternative categorical limit. Because the Leather Tanning and Finishing pretreatment standards do not include self-monitoring requirements, the Control Authority will establish appropriate self-monitoring requirements.

#### 4.4.3. Application of the CWF

The combined wastestream formula are presented in Table 4.1. Table 4.2 presents three examples of how the CWF is used to calculate alternative limits for specific leather tanning and finishing operations. Before using the CWF, remember that when two or more regulated wastestreams are mixed prior to treatment, it is necessary to determine which pretreatment regulation applies to each regulated wastestream before they are mixed. For additional information on categorical pretreatment standards and combined wastestream formula, refer to the manual entitled "Guidance Manual for the Use of Production-based Pretreatment Standards and the Combined Wastestream Formula" (September 1985). For calculation of the total toxic organics (TTO) limits, refer to the manual entitled, "Guidance Manual for Implementing Total Toxic Organic (TTO) Pretreatment Standards (September 1985).

#### 4.5 Removal Credits

On April 30, 1986 the United States Court of Appeals for the Third Circuit upheld the Natural Resources Defense Council's challenge to EPA's



TABLE 4.1  
COMBINED WASTESTREAM FORMULAS

Alternative Concentration Limit Formula:

$$C_t = \left( \frac{\sum_{i=1}^N C_i F_i}{\sum_{i=1}^N F_i} \right) \times \left( \frac{F_t - F_d}{F_t} \right)$$

- $C_t$  - alternative concentration limit for the pollutant
- $C_i$  - Categorical Pretreatment Standard concentration limit for the pollutant in regulated stream  $i$
- $F_i$  - average daily flow (at least 30 day average) of regulated stream  $i$
- $F_d$  - average daily flow (at least 30 day average) of dilute wastestream(s)
- $F_t$  - average daily flow (at least 30 day average) through the combined treatment facility (including regulated, unregulated and dilute wastestreams)
- $N$  - total number of regulated streams

Alternate Mass Limit Formula

$$M_t = \left( \sum_{i=1}^N M_i \right) \times \left( \frac{F_t - F_d}{\sum_{i=1}^N F_i} \right)$$

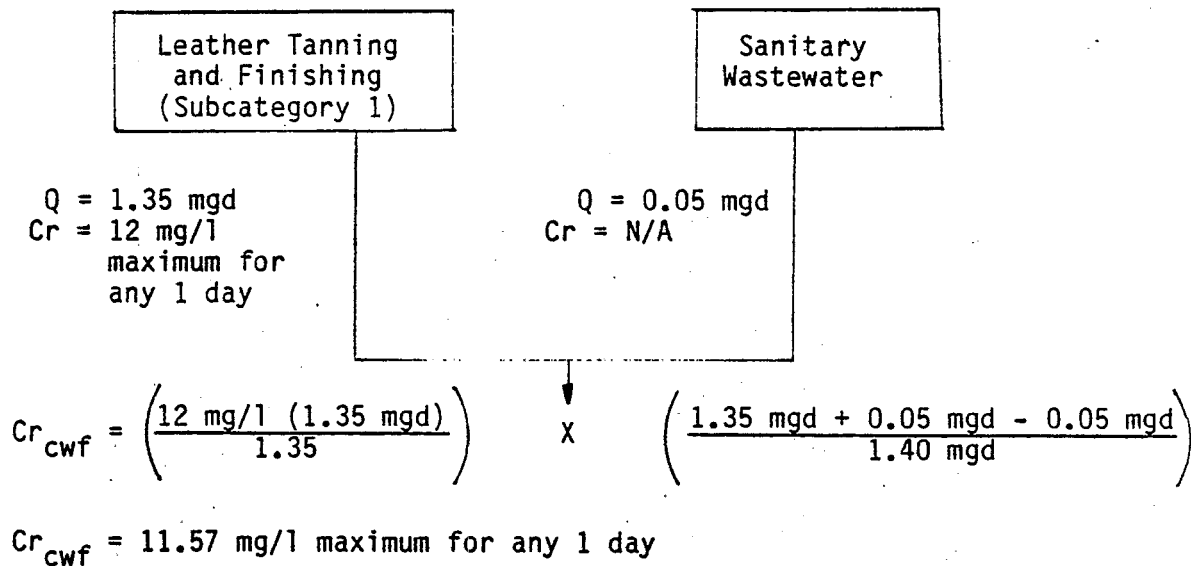
- $M_t$  - alternative mass limit for the pollutant
- $M_i$  - Categorical Pretreatment Standard Production-based limit for the pollutant in regulated stream  $i$
- $F_i$  - average daily flow (at least 30 day average) of regulated stream  $i$
- $F_d$  - average daily flow (at least 30 day average) of dilute wastestream(s)
- $F_t$  - average daily flow (at least 30 day average) through the combined treatment facility (including regulated, unregulated and dilute wastestreams)
- $N$  - total number of regulated streams.

TABLE 4.2

## EXAMPLE A

COMBINED WASTESTREAM FORMULA EXAMPLE CALCULATION  
WITH CONCENTRATION-BASED LIMITS

Alternative discharge limit for a leather tanning and finishing facility after November 25, 1985 (compliance date for leather tanning and finishing).



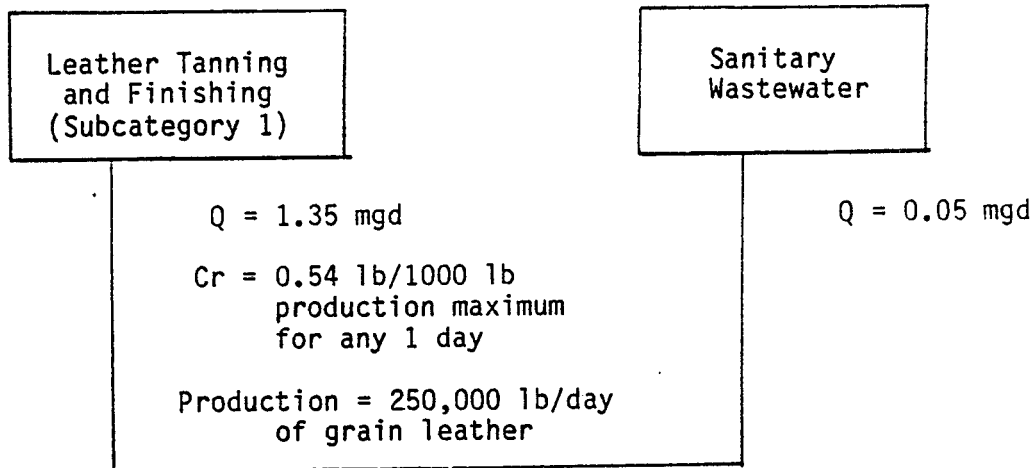
Note: Due to dilution from sanitary wastewater, the applicable Cr limit, 12 mg/l, is reduced to 11.57 mg/l.

TABLE 4.2 (Continued)

EXAMPLE B

COMBINED WASTESTREAM FORMULA EXAMPLE  
CALCULATION WITH ALTERNATE PRODUCTION-BASED LIMITS

Alternative Mass based discharge limit for a leather tanning and finishing facility after November 25, 1985 (compliance date for leather tanning and finishing).



$$Cr_{cwf} = \left( \frac{0.54 \text{ lb}}{1000 \text{ lb prod.}} \right) \left( \times 250,000 \text{ lb prod.} \right) \times \left( \frac{1.40 - 0.05}{1.35} \right)$$

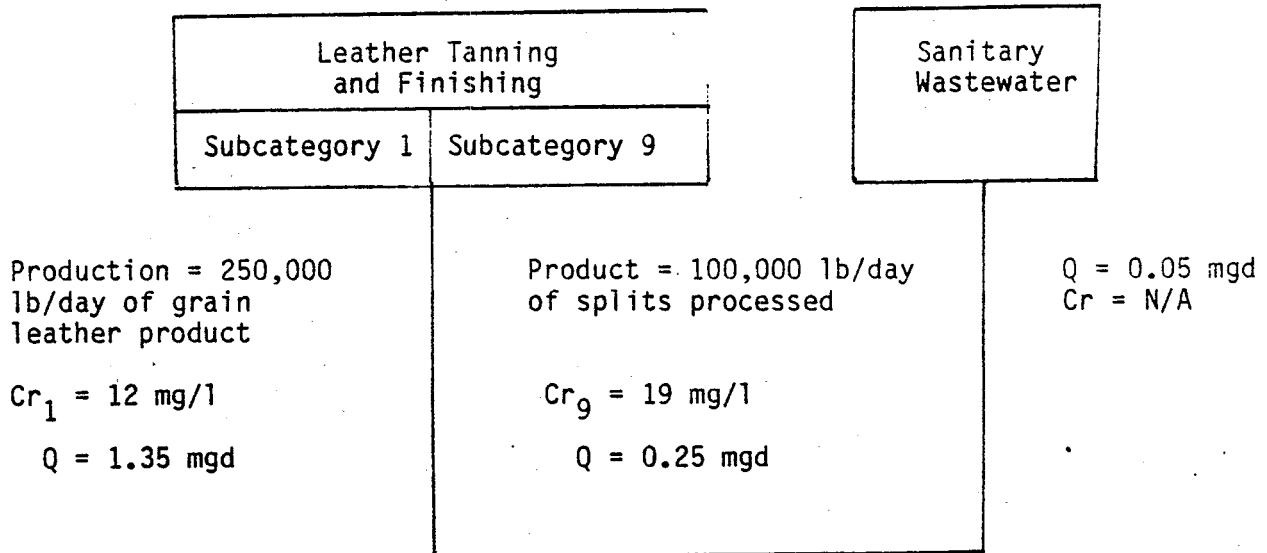
$$Cr_{cwf} = 135 \text{ lb/day maximum for any 1 day}$$

TABLE 4.2 (Continued)

EXAMPLE C

COMBINED WASTESTREAM FORMULA EXAMPLE CALCULATION  
FOR INTEGRATED (MULTI-SUBCATEGORY) FACILITY

Alternative discharge limit for a multi-subcategory integrated facility after November 25, 1985 (compliance date for leather and finishing).



$$Cr_{cwf} = \left( \frac{12(1.35) + 19(0.25)}{1.35 + 0.25} \right) \times \left( \frac{1.65 - 0.05}{1.65} \right)$$

$Cr_{cwf} = 12.7 \text{ mg/l}$  maximum for any 1 day

Alternate Production-based Limit:

$$Cr_{cwf} = \left[ \frac{(250,000 \text{ lb/day} \times 0.54 \text{ lb/1000 lb}) + (100,000 \text{ lb/day} \times 0.47 \text{ lb/1000 lb})}{\text{Subcategory 1} \quad \text{Subcategory 9}} \right] \times \left[ \frac{1.65 - 0.05}{1.60} \right]$$

$Cr_{cwf} = 135 + 47 = 182 \text{ lbs}$  maximum for any 1 day

removal credits regulation (NRDC vs. EPA, No. 84-3530). The Court struck down the amended regulation on four separate grounds:

- (1) EPA's new definition of a POTW's "consistent removal" rate failed to implement the requirements of the Clean Water Act and therefore was invalid;
- (2) EPA's failed to justify deletion of the previously promulgated combined sewer overflow adjustment;
- (3) EPA's provision specifying the modification and withdrawal process of a POTW's removal credits was illegal; and
- (4) EPA cannot, in the absence of §405 sludge regulations, authorize the granting of removal credits to POTWs under §307(b)(1) of the Act.

EPA is determining what course of action to take in light of this decision. The immediate effect of the court ruling, however, is that no further consideration can be given to removal credit applications. As soon as it determines the full scope and effect of this decision and determines its course of action, EPA will provide guidance through its Regional Pretreatment Coordinators to the POTWs impacted by this decision. EPA recommends that you periodically contact your Control Authority or the appropriate EPA Regional Office for any future guidance on the status of the removal credits regulation

#### 4.6 Fundamentally Different Factors Variance

A request for a fundamentally different factors (FDF) variance is a mechanism by which a categorical pretreatment standard may be adjusted on a case-by-case basis. If an indirect discharger, a POTW, or any interested person believes that the factors relating to a specific indirect discharger are fundamentally different from those factors considered during development of the relevant categorical pretreatment standard and that the existence of those factors justifies a different discharge limit from that specified in the Categorical Standard, then they may submit a request to EPA for such a variance (See 40 CFR 403.13).

#### 4.7 LOCAL LIMITS

Local limits are numerical pollutant concentration or mass-based values that are developed by a POTW for controlling the discharge of conventional, non-conventional, or toxic pollutants from indirect sources. They differ from national categorical pretreatment standards in that categorical pretreatment standards are developed by EPA and are based on the demonstrated performance of available pollutant control technologies for specific categorical industries. These technology-based categorical standards do not consider local environmental criteria or conditions, but are developed to assure that each industry within a specified category meets a minimum discharge standard that is consistent for all POTWs across the United States. Local limits, on the other hand, are developed to address specific localized impacts on POTWs and their receiving waters. Local limits are typically designed to protect the POTW from:

- Introduction of pollutants into the POTW that could interfere with the operation
- Pass-through of inadequately treated pollutants that could violate a POTW's NPDES permit or applicable water quality standards
- Contamination of a POTW's sludge, which would limit sludge uses or disposal practices.

Local limits, as the name implies, take into consideration the factors that are unique to a POTW, whereas categorical pretreatment standards are developed only for a general class of industrial dischargers. Local limits are required under 40 CFR 403.5. For more information on the minimum local limit requirements for POTWs with approved pretreatment programs and the relationship between local limits and categorical standards, refer to the memorandum signed by Rebecca Hanmer on August 5, 1985 entitled "Local Limit Requirements for POTW Pretreatment Program".

To assist municipalities in developing defensible and technically sound numerical effluent limits, EPA has prepared general guidelines on limit development in its document "Guidance Manual for POTW Pretreatment Program Development." Appendix L of the manual lists the general methodology,

required formulas, and typical environmental criteria used to develop local limits. The manual is available from EPA Regional offices and delegated States and should be carefully followed when developing local limits. A more detailed guidance manual for local limit development is currently under development. The general methodology includes the following four steps:

- Step 1 - Determine the maximum headworks loading (for each specific pollutant) that will assure that the objectives of the pretreatment program are met.
- Step 2 - Calculate the allowable loading to the POTW by subtracting the uncontrollable portion of pollutant discharge to the POTW (from domestic, commercial, and infiltration/inflow sources) from the total headworks loading value.
- Step 3 - Distribute the controllable loading to industrial users through an allocation process.
- Step 4 - Derive specific local limits from the allocation results.

This four-step process must be followed for each pollutant that the POTW determines may need a specific local limit. As a general rule, the limit setting analysis should be performed for all pollutants that are discharged to the POTW in significant quantities. The POTW can identify pollutants of concern through its industrial waste survey. A procedure for evaluating industrial waste survey results is included in the EPA guidance manual mentioned above.

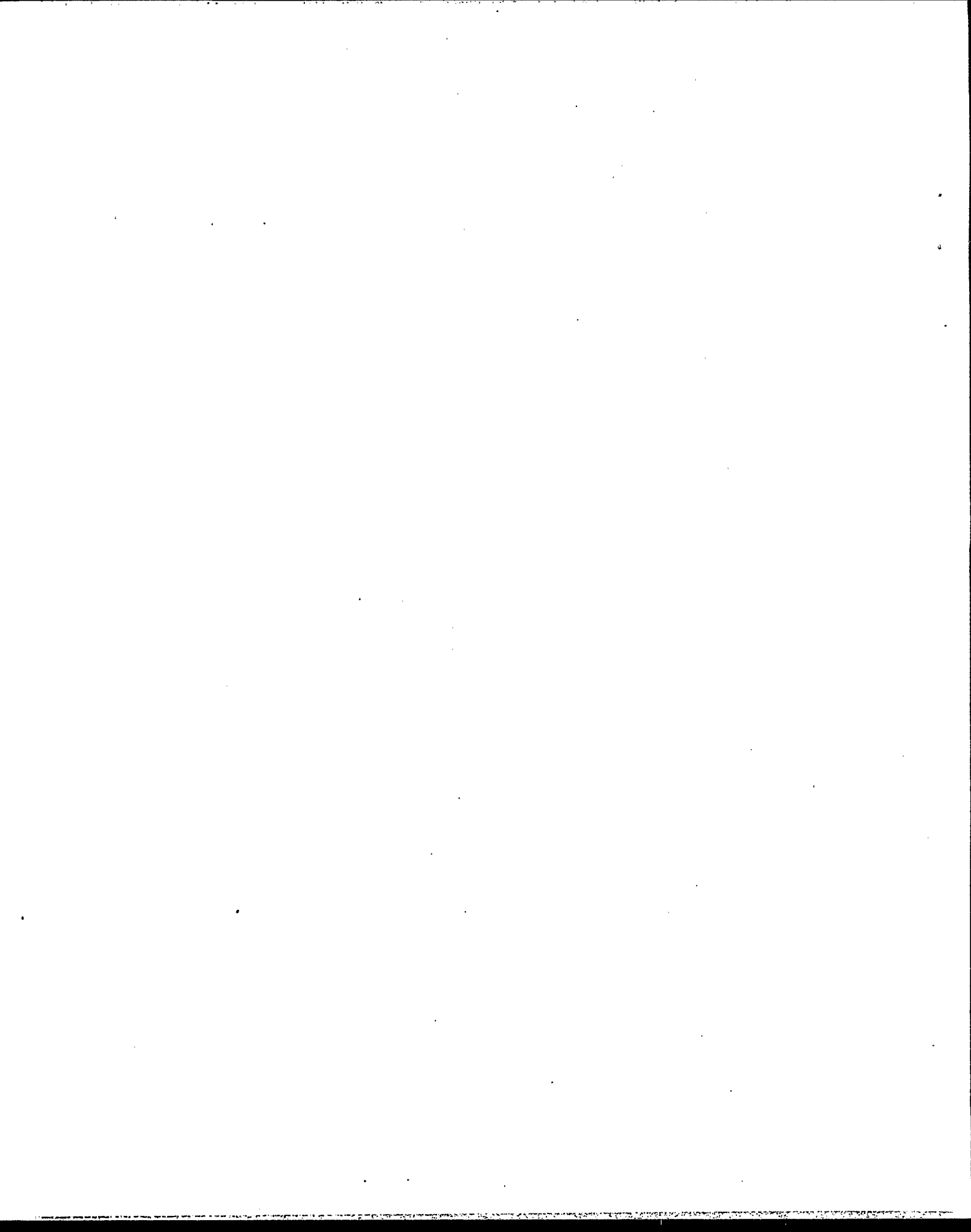
To assist POTWs with the development of local limits, EPA has also developed a computer program that incorporates the general methodology required to develop local limits and performs a substantial number of the calculations required to develop these limits. This computer program has the following capabilities.

- Performs the four-step limit setting analysis on microcomputer or mainframe
- Screens input data provided by the POTW
- Supplements POTW data with built-in files containing data on industrial and municipal wastewater characteristics, POTW removal rates and POTW inhibition values

- Allocates controllable pollutant loads using several different methodologies
- Compares calculated local limits to EPA categorical standards.

POTWs may obtain information on this computer program by contacting the EPA Regional office. Instructions are available on how to obtain and use the computer program as well as how to gain access to a computer system that supports it.





REFERENCES

Leather Tanning Regulations

Federal Register Notice

Final PSNS Regulations Promulgated	4/9/74	39 FR 12958
Amended (Promulgated PSES)	3/23/77	42 FR 15696
Promulgated Revised PSES and PSNS	11/23/82	47 FR 52848
Corrected and Amended (Typographical errors and sulfide applicability date)	6/30/83	48 FR 30116
Amended (Sulfide applicability)	7/8/83	48 FR 31404
Corrected (Sulfide PSES effective dates)	7/15/83	48 FR 32346
Corrected (Sulfide PSES effective dates)	8/5/83	48 FR 35649
Amended (Compliance Date)	9/15/83	48 FR 41410
Settlement Agreement, dated December 11, 1984		

General Pretreatment Regulations

40 CFR Part 403	1/15/83	46 FR 9404
Amended 40 CFR Part 403	4/17/84	49 FR 21037
Amended 40 CFR Part 403 (Removal Credits)	8/3/84	49 FR 31212
Amended 40 CFR Part 403 (FDF Provision)	9/25/85	50 FR 38809

Technical Development Documents

		<u>EPA Document No.</u>	<u>NTIS or GPO No.</u>
Final Development Document - Leather Tanning	November 1982	440/1-82/016	PB83-172593
Guidance Manual for POTW Pretreatment Program Development	October 1983	--	--
Procedures Manual for Reviewing a POTW Pretreatment Program Submission	October 1983	--	--
Guidance Manual for Preparation of Removal Credits Applications	September 1985	--	--

<u>Technical Development Documents (Continued)</u>		<u>EPA Document No.</u>	<u>NTIS or GPO No.</u>
Guidance Manual for Implementing Total Toxic Organics (TTO) Pretreatment Standards	September 1985	--	--
Guidance Manual for the Use of Production-based Pretreatment Standards and the Combined Wastestream Formula	September 1985	--	--

Miscellaneous

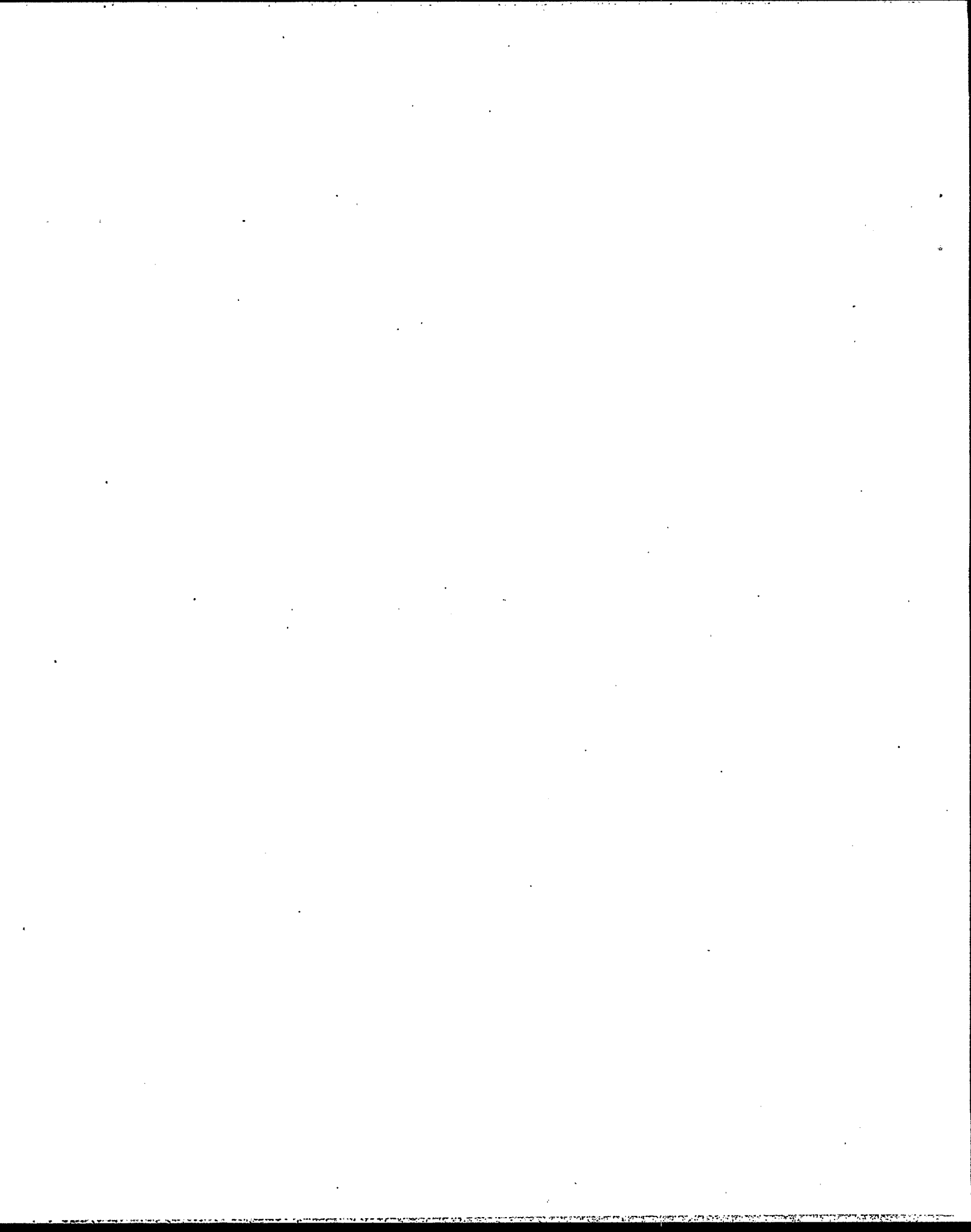
RCRA Information for Publicly  
Owned Treatment Works                      September 1985

Local Limits Requirements for POTW Pretreatment Programs, memorandum signed by  
Rebecca Hanmer on August 5, 1985.

Copies of the technical and economic documents may be obtained from  
the National Technical Information Services, Springfield, VA 22161.  
(703/487-4650). Pretreatment Program Manuals may be obtained from U.S. EPA,  
Permits Division (EN-336), Washington, DC 20460.

APPENDIX A

EXPANDED REVIEW CRITERIA FOR  
LEATHER TANNING SULFIDE WAIVER APPLICATIONS



## Introduction

Publicly owned treatment works (POTWs) with industrial users (IUs) regulated by the 40 CFR 425 Leather Tanning and Finishing Regulations have the option to request that the categorical pretreatment standard for sulfide be waived for tanners provided that the user's sulfide discharge does not interfere with operations of the treatment works. The POTW must provide a statement that certifies and supports to the Regional Water Division Director the noninterference claim.

As part of the waiver review process, the Region will determine whether the applicant has complied with the public noticing and certification requirements of Sections 425.04(b) and (c). The adequacy of the certification will be determined by comparing the information in the applicant's submittal to the criteria as listed below. Section 425.04(b) lists four general factors on which the POTW must report. Since these factors are general in nature and tannery sulfide discharges may have significant environmental impact, the Region will be using more specific criteria to assess whether this discharge would have a deleterious effect on the treatment works' operations. If submittals for the waiver requests do not contain sufficient information as specified by the criteria, the POTWs will be required to provide the Region with further data for review before a formal determination is issued on the request.

## Criteria

- A. Provide the following information for each of the tannery facilities for which the sulfide waiver is proposed to be granted.
  1. Description of tanning operations. (NOTE: If the user engages in unhairing operations specify if beamhouse (hair pulp or hair save) and tanyard (pickling) processes are performed.)
  2. The applicable subpart that would apply to the user's operations according to the Leather Tanning Subcategories.
  3. The present, past, and maximum process capacity (hides/day) of the user.
  4. Diagram of tanning and finishing processes and wastewater flows, especially for unhairing and pickling operations.

5. Specify whether spent liquors are discharged or recycled.
  6. Characteristics of waste discharge including:
    - a. Analytical data on sulfide and other sulfur compounds such as sulfates, etc.
    - b. pH (average and range) of wastestreams.
    - c. volume of discharge (average and maximum, GPD).
  7. Specify whether the plant's discharge schedule is continuous, batch, etc.
  8. What, if any, pretreatment is employed at the plant especially in regards to sulfide and pH?
  9. Are the facilities regulated by any local limitations or prohibited discharges?
    - Specify the mechanism (i.e. permits, contract, order, ordinance, etc.).
  10. If the above does apply, have there been any instances where the discharger did not meet these limitations?
  11. Provide a map of the treatment service area illustrating the points of discharge of the tanners.
- B. The following items will be considered under factors (1)-(4) of Section 425.04(b).
- 425.04(b)(1)
- "The presence and characteristics, of other industrial wastewaters which can increase or decrease sulfide concentrations, pH or both."
- a. When reporting other industries that have the potential to contribute to the sulfide or low pH problem specify:
    1. The operations of the facility that generate these wastes.
    2. Wastewater discharge volume.
    3. Wastewater characteristics such as pH and sulfide/sulfur content.
    4. Discharge schedule (batch, continuous, etc.).
  - b. If there are other tanning facilities in the treatment system that are not requesting the sulfide waiver, indicate whether they have the potential to contribute to the sulfide or low pH problem. If they do have this potential, submit information as required in "a" above about the facilities.
  - c. On a map of the treatment service area, indicate the location of industries that do have the potential to contribute to sulfide and pH problems.

425.04(b)(2)

"The characteristics of the sewer/interceptor collection system which either minimize or enhance opportunities for release of hydrogen sulfide gas."

- a. Is the sewage system free-flowing?
  1. Are there stagnant or dead spots in the system after points of contribution from tanners?
  2. Are these areas aerobic or anaerobic?
- b. Are personnel that would enter these areas for sampling purposes, etc., using confined space entry procedures and three-way gas monitors as precautionary measures?
- c. Have there been any reports (not necessarily confirmed) of worker's health problems that could be related to hydrogen sulfide exposure? Symptoms could include eye irritation, pulmonary distress, headaches and dizziness.
- d. Have there been complaints of odor problems ("rotten eggs") along the treatment lines?
- e. Provide recent survey information on the sewer lines to illustrate whether damage has occurred from the conversion of hydrogen sulfide to sulfuric acid.

425.04(b)(3)

"The characteristics of the receiving POTW headworks, preliminary and primary treatment systems, and, sludge holding and dewatering facilities which either minimize or enhance opportunities for release of hydrogen sulfide gas."

- a. Are the treatment facilities enclosed or well ventilated?
- b. Does the system have a long hydraulic detention time?
- c. Does the municipality have an influent/effluent discharge standard for sulfide or pH? If so, what are they? If not, are any being proposed?
- d. Are any of the tanners requesting a waiver for facilities located within another township or municipality outside your legal jurisdiction but discharging to your system?
- e. What levels of sulfide are entering and being discharged from the POTW (average and maximum)?
- f. Provide a 5-year historical review of sulfide related interference problems. This should address corrosion, hydrogen sulfide toxicity to the system, problems with sludge disposal because of odor, permit violations and any other POTW interference.



- g. Have there been complaints of odor problems ("rotten eggs") at the treatment plant?
- h. Have there been any reports of worker's health problems or deaths that could be related to hydrogen sulfide exposure at the treatment works?
- i. Has OSHA established ambient air limits for hydrogen sulfide at the treatment plant?

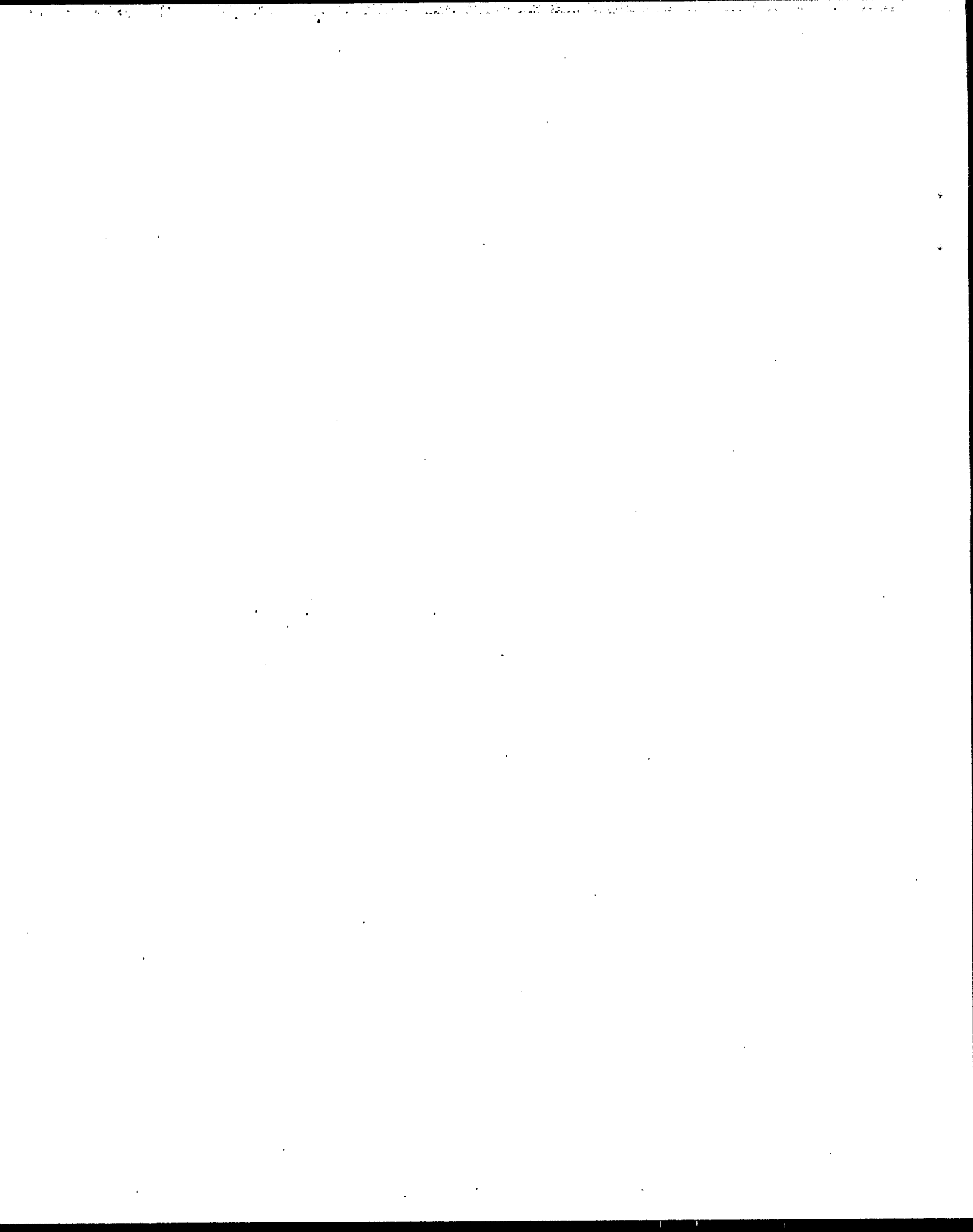
425.04 (b)(4)

"The occurrence of any prior sulfide related interference as defined by 425.02(j)."

Section 425.02(j) defines "Interference" as "the discharge of sulfides in quantities which can result in human health standards and/or risks to human life, and an inhibition or disruption of POTW as defined in 40 CFR 403.3(j)."

This definition of interference should be noted when formulating responses to the above inquiries.

APPENDIX B  
SULFIDE ANALYTICAL METHOD



## APPENDIX B

### I. SULFIDE ANALYTICAL METHODS

"Sulfide" shall mean total sulfide as measured by the potassium ferricyanide titration method or the modified Monier-William method described below.

#### (a) Applicability

The potassium ferricyanide titration method described in §425.03 of 40 CFR 425\* shall be used whenever practicable for the determination of sulfide in wastewater discharged by plants operating in all subcategories except the hair save or pulp, non-chrome tan, retan-wet finish subcategory (Subpart C, see §425.30). In all other cases, the modified Monier-Williams method as described in Appendix B to 40 CFR Part 425 in the proposed amendments shall be used as an alternative to the potassium ferricyanide titration method for the determination of sulfide in wastewaters discharged by plants operating in all subcategories except Subpart C.

The modified Monier-Williams method as described in Appendix B to 40 CFR Part 425 in the proposed amendments shall be used for the determination of sulfide in wastewaters discharged by plants operating in the hair save or pulp, non-chrome tan, retan-wet finish subcategory (Subpart C, see §425.30).

#### (b) Potassium Ferricyanide Titration Method

The potassium ferricyanide titration method is based on method SLM 4/2 described in Official Method of Analysis, Society of Leather Trades' Chemists, Fourth Revised Edition, Redbourn, Herts., England, 1965.

(1) Outline of Method. The buffered sulfide solution is titrated with standard potassium ferricyanide solution in the presence of ferrous dimethylglyoxime ammonia complex. The sulfide is oxidized to sulfur. Sulfite interferes and must be precipitated with barium chloride. Thiosulfate is not titrated under the conditions of the determination. (Charlot, Ann. chim. anal., 1945, 27, 153; Booth, J. Soc. Leather Trades' Chemists, 1956, 40, 238).

(2) Apparatus. Burette, 10 ml.

(3) Reagents.

(A) Preparation of 0.02N potassium ferricyanide: Weigh to the nearest tenth of a gram 6.6 g of analytical reagent grade potassium ferricyanide and dissolve in 1 liter distilled water. Store in an amber bottle in the dark. Prepare fresh each week.

(B) Standardization of ferricyanide solution: Transfer 50 ml of solution to a 250 ml Erlenmeyer flask. Add several crystals of potassium iodide (about 1 g), mix gently to dissolve, add 1 ml

\*Will be found in Appendix A to 40 CFR Part 425 of the proposed amendments implementing the settlement agreement.

of 6N hydrochloric acid, stopper the flask, and swirl gently. Let stand for two minutes, add 10 ml of a 30 percent zinc sulfate solution, and titrate the mixture containing the gelatinous precipitate with standardized sodium thiosulfate or phenylarsine oxide titrant in the range of 0.025-0.050N. Add 1 ml of starch indicator solutions after the color has faded to a pale yellow, and continue the titration to the disappearance of the blue color. Calculate the normality of the ferricyanide solution using the equation:

$$\text{Normality of Potassium Ferricyanide } [K_3Fe(CN)_6] = \frac{(\text{ml of thiosulfate added}) (\text{normality of thiosulfate})}{\text{ml of } K_3Fe(CN)_6}$$

- (C) Preparation of 6M ammonium chloride buffer, pH 9.3: Dissolve 200 g ammonium chloride in approximately 500 ml distilled water, add 200ml 14M reagent grade ammonium hydroxide and make up to 1 liter with distilled water. The buffer should be prepared in hood. Store in a tightly stoppered container.
- (D) Preparation of 0.05M barium chloride solution: Dissolve 12-13 g barium chloride dihydrate in 1 liter of distilled water.
- (E) Preparation of ferrous dimethylglyoxime indicator solution: Mix 10 ml 0.6 percent ferrous sulfate, 50 ml 1 percent dimethylglyoxime in ethanol, and 0.5 ml concentrated sulfuric acid.
- (F) Preparation of stock sulfide standard, 1000 ppm: Dissolve 2.4 g reagent grade sodium sulfide in 1 liter of distilled water. Store in a tightly stoppered container. Diluted working standards must be prepared fresh daily and their concentrations determined by EPA test procedure 376.1 immediately prior to use [see 40 CFR 136.3, Table IB, parameter 66 (49 FR 43234, October 26, 1984, with correction notice at 50 FR 690, January 4, 1985)].
- (G) Preparation of 10N NaOH: Dissolve 400 g of analytical reagent grade NaOH in 1 liter distilled water.

(4) Sample Preservation and Storage.

Samples are to be field filtered (gravity or pressure) with coarse filter paper (Whatman 4 or equivalent) immediately after collection. Filtered samples must be preserved by adjustment to pH>12 with 10N NaOH. Sample containers must be covered tightly and stored at 4°C until analysis. Samples must be analyzed within 48 hours of collection. If these procedures cannot be achieved, it is the laboratory's responsibility to institute quality control procedures that will provide documentation of sample integrity.

(5) Procedure.

- (A) Transfer 100 ml of sample to be analyzed, or a suitable portion containing not more than 15 mg sulfide supplemented to 100 ml with distilled water, to a 250 ml Erlenmeyer flask.
- (B) Adjust the sample to pH 8.5-9.5 with 6N HCl.
- (C) Add 20 ml of 6M ammonium chloride buffer (pH 9.3), 1 ml of ferrous dimethylglyoxime indicator, and 25 ml of 0.05 M barium chloride. Mix gently, stopper, and let stand for 10 minutes.
- (D) After 10 minutes titrate with standardized potassium ferricyanide to disappearance of pink color. The endpoint is reached when there is no reappearance of the pink color after 30 seconds.

(6) Calculation and Reporting of Results.

(A) 
$$\text{mg/l Sulfide} = \frac{A \times B \times 16,000}{\text{vol. in ml of sample titrated}}$$

where A = volume in ml of potassium ferricyanide solution used  
and B = normality of potassium ferricyanide solution.

- (B) Report results to two significant figures.

(7) Quality Control.

- (A) Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of replicate and spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within precision and accuracy limits expected of the methods.
- (B) Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method by performing the following operations.
  - (i) Perform four replicate analyses of a 20mg/l sulfide standard prepared in distilled water [see (3)(F)].
  - (ii) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented below. These criteria must be met or exceeded before sample analyses can be initiated. A clean water standard must be analyzed with each sample set and the established criteria met for the analysis to be considered under control.

Clean water precision and accuracy acceptance limits:  
For distilled water samples containing from 5 mg/l to 50 mg/l sulfide, the mean concentration from four replicate analyses must be within the range of 50 to 110 percent of the true value.

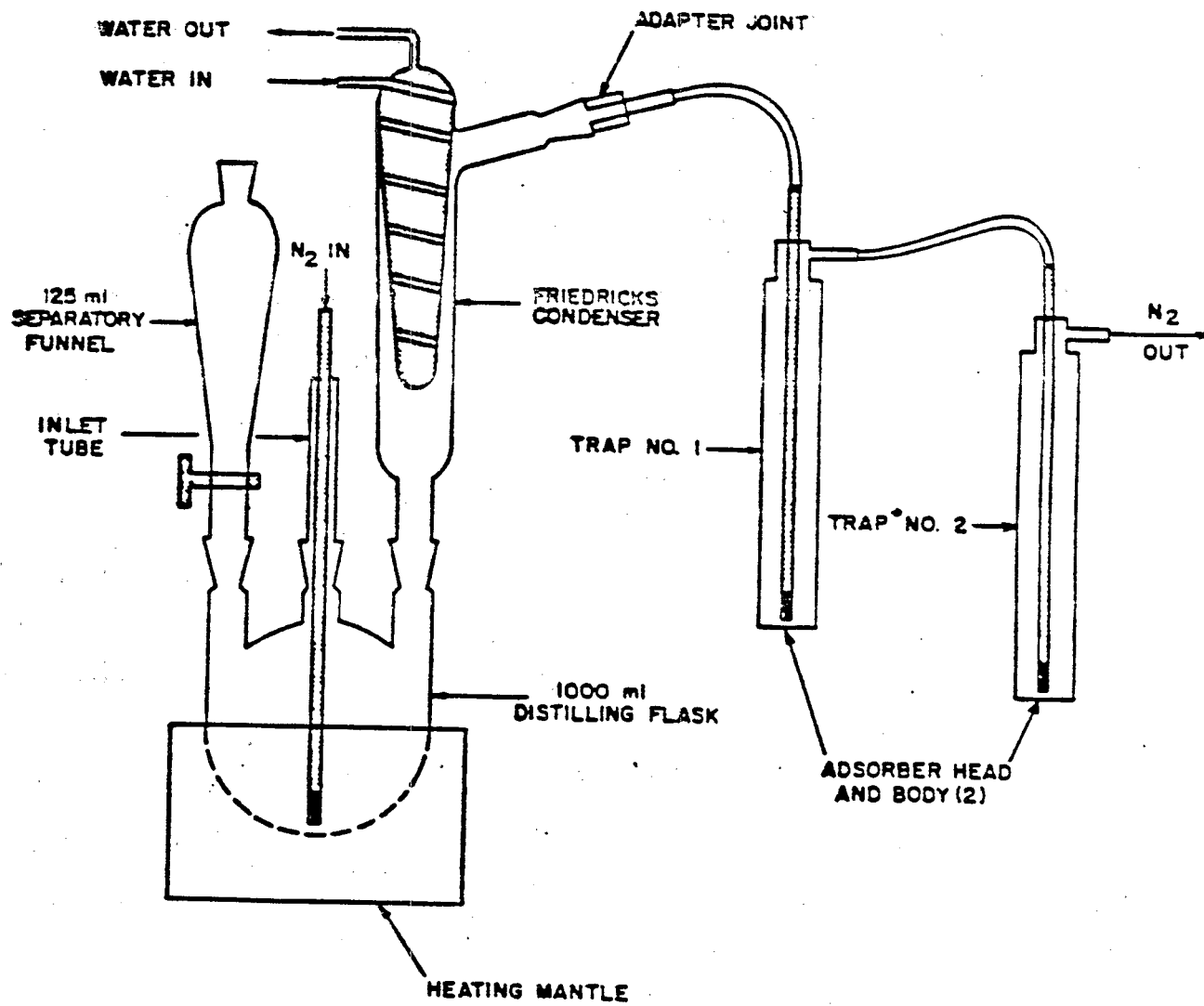
- (C) The method detection limit (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in Appendix B to 40 CFR Part 136 (49 FR 4324, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985). The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte.
- (D) A minimum of one spiked and one duplicate sample must be performed for each analytical event, or five percent spikes and five percent duplicates when the number of samples per event exceeds twenty. Spike levels are to be at the MDL [see (7)(C)] for MDL samples, and at  $x$  where  $x$  is the concentration found if in excess of the MDL. Spike recovery must be 40 to 120 percent for the analysis of a particular matrix type to be considered valid. If a sample or matrix type provides performance outside these acceptance limits, the analyses must be repeated using the modified Monier-Williams procedure described in Appendix B to 40 CFR Part 425 in the proposed amendments.
- (E) Report results in mg/liter. When duplicate and spiked samples are analyzed, report all data with the sample results.

(c) Modified Monier-Williams Method.

(1) Outline of Method.

Hydrogen sulfide is liberated from an acidified sample by distillation and purging with nitrogen gas ( $N_2$ ). Sulfur dioxide interference is removed by scrubbing the nitrogen gas stream in a pH 7 buffer solution. The sulfide gas is collected by passage through an alkaline hydrogen peroxide scrubbing solution in which it is oxidized to sulfate. Sulfate concentration in the scrubbing solution is determined by either EPA gravimetric test procedure 375.3 or EPA turbidimetric test procedure 375.4 [see 40 CFR 136.3, Table IB, parameter 65 (40 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)].

(2) Apparatus. (See Figure 1) Catalogue numbers are given only to provide a more complete description of the equipment necessary, and do not constitute a manufacturer or vendor endorsement.



**FIGURE 1**  
**EQUIPMENT ASSEMBLY**



- (A) Heating mantle and control (VWR Cat. No. 33752-464)
  - (B) 1000 ml distilling flask with three 24/40 joints (VWR Cat. No. 29280-215)
  - (C) Friedrichs condenser with two 24/40 joints (VWR Cat. No. 23161-009)
  - (D) 125 ml separatory funnel with 24/40 joint (VWR Cat. No. 30357-102)
  - (E) Inlet tube with 24/40 joint (VWR Cat. No. 33057-105)
  - (F) Adapter joint 24/40 to 19/38 (VWR Cat. No. 62905-26)
  - (G) Adsorber head (2 required) (Thomas Cat. No. 9849-R29)
  - (H) Absorber body (2 required) (Thomas Cat. No. 9849-R32)
  - (I) Laboratory vacuum pump or water aspirator
- (3) Reagents.
- (A) Potassium hydroxide, 6N: Dissolve 340 g of analytical reagent grade KOH in 1 liter distilled water.
  - (B) Sodium hydroxide, 6N: Dissolve 240 g of analytical reagent grade NaOH in 1 liter distilled water.
  - (C) Sodium hydroxide, 0.03N: Dilute 5.0 ml of 6N NaOH to 1 liter with distilled water.
  - (D) Hydrochloric acid, 6N: Dilute 500 ml of concentrated HCl to 1 liter with distilled water.
  - (E) Potassium phosphate stock buffer, 0.5M: Dissolve 70 g monobasic potassium phosphate in approximately 800 ml distilled water. Adjust pH to  $7.0 \pm 0.1$  with 6N potassium hydroxide and dilute to 1 liter with distilled water. Stock solution is stable for several months at 4°C.
  - (F) Potassium phosphate buffer, 0.05M: Dilute 1 volume of 0.5M potassium phosphate stock buffer with 9 volumes of distilled water. Solution is stable for 1 month at 4°C.
  - (G) Alkaline 3 percent hydrogen peroxide. Dilute 1 volume of 30 percent hydrogen peroxide with 9 volumes of 0.03N NaOH. Prepare this solution fresh each day of use.
  - (H) Preparation of stock sulfide standard, 1000 ppm: Dissolve 2.4 g reagent grade sodium sulfide in 1 liter of distilled water. Store in a tightly stoppered container. Diluted working standards must be prepared fresh daily and their concentrations determined by EPA test procedure 376.1

immediately prior to use [see CFR 136.3, Table IB, parameter 66 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)].

(4) Sample Preservation and Storage.

Preserve unfiltered wastewater samples immediately after collection by adjustment to  $\text{pH} > 9$  with 6N NaOH and addition of 2 ml of 2N zinc acetate per liter. This amount of zinc acetate is adequate to preserve 64 mg/l sulfide under ideal conditions. Sample containers must be covered tightly and stored at  $4^{\circ}\text{C}$  until analysis. Samples must be analyzed within seven days of collection. If these procedures cannot be achieved, it is the laboratory's responsibility to institute quality control procedures that will provide documentation of sample integrity.

(5) Procedure. (See Figure 1 for apparatus layout)

- (A) Place 50 ml of 0.05M pH 7.0 potassium phosphate buffer in Trap No. 1.
- (B) Place 50 ml of alkaline 3 percent hydrogen peroxide in Trap No. 2.
- (C) Sample introduction and  $\text{N}_2$  prepurge: Gently mix sample to be analyzed to resuspend settled material, taking care not to aerate the sample. Transfer 400 ml of sample, or a suitable portion containing not more than 20 mg sulfide diluted to 400 ml with distilled water, to the distillation flask. Adjust the  $\text{N}_2$  flow so that the impingers are frothing vigorously but not overflowing. Vacuum may be applied at the outlet of Trap No. 2 to assist in smooth purging. The  $\text{N}_2$  inlet tube of the distillation flask must be submerged deeply in the sample to ensure efficient agitation. Purge the sample for 30 minutes without applying heat. Test the apparatus for leaks during the prepurge cycle (Snoop or soap water solution).
- (D) Volatilization of  $\text{H}_2\text{S}$ : Interrupt the  $\text{N}_2$  flow (and vacuum) and introduce 100 ml of 6N HCl to the sample using the separatory funnel. Immediately resume the gas flow (and vacuum). Apply maximum heat with the heating mantle until the sample begins to boil, then reduce heat and maintain gentle boiling and  $\text{N}_2$  flow for 30 minutes. Terminate the distillation cycle by turning off the heating mantle and maintaining  $\text{N}_2$  flow through the system for 5 to 10 minutes. Then turn off the  $\text{N}_2$  flow (and release vacuum) and cautiously vent the system by placing 50 to 100 ml of distilled water in the separatory funnel and opening the stopcock carefully. When the bubbling stops and system is equalized to atmospheric pressure, remove the separatory funnel. Extreme care must be exercised in terminating the distillation cycle to avoid flash-over, draw-back, or violent steam release.

- (E) Analysis: Analyze the contents of Trap No. 2 for sulfate according to either EPA gravimetric test procedure 375.3 or EPA turbidimetric test procedure 375.4 [see 40 CFR 136.3, Table IB, parameter 65 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)]. Use the result to calculate mg/l in the wastewater sample.

(6) Calculations and Reporting of Results.

- (A) Gravimetric procedure:

$$\text{mg sulfide/l} = \frac{(\text{mg BaSO}_4 \text{ collected in Trap No. 2}) \times (137)}{\text{Volume in ml of waste sample distilled}}$$

- (B) Turbidimetric procedure:

$$\text{mg sulfide/l} = \frac{A \times B \times 333}{\text{volume in ml of waste sample distilled}}$$

where A = mg/l of sulfate in trap no. 2  
and B = liquid volume in liters in trap no. 2

- (C) Report results to two significant figures.

(7) Quality Control.

- (A) Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of replicate and spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within precision and accuracy limits expected of the method.
- (B) Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method by performing the following operations.
- (i) Perform four replicate analyses of a 20 mg/l sulfide standard prepared in distilled water (see(3)(H)).
- (ii) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented below. These criteria must be met or exceeded before sample analyses can be initiated. A clean water standard must be analyzed with each sample set and the

established criteria met for the analysis to be considered under control.

Clean water precision and accuracy acceptance limits: For distilled water samples containing from 5 to 50 mg/l sulfide, the mean concentration from four replicate analyses must be within the range of 72 to 114 percent of the true value.

- (C) The method detection limit (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in Appendix B to 40 CFR Part 135 (40 FR 4324, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985). The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte.
- (D) A minimum of one spiked and one duplicate sample must be run with each analytical event, or five percent spikes and five percent duplicates when the number of samples per event exceeds twenty. Spike levels are to be at the MDL (See Section (7)(C)) for MDL samples, and at x when x is the concentration found if in excess of the MDL. Spike recovery must be 60 to 120 percent for the analysis of a particular matrix type to be considered valid.
- (E) Report all results in mg/liter. When duplicate and spike samples are analyzed, report all data with the sample results.