United States Environmental Protection Agency Industrial Environmental Research Laboratory Cincinnati OH 45268 EPA-600/2-78-1 October 1978



# Assessment of Potential Toxic Releases from Leather Industry Dyeing Operations



# **RESEARCH REPORTING SERIES**

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

- 1. Environmental Health Effects Research
- 2. Environmental Protection Technology
- 3 Ecological Research
- 4. Environmental Monitoring
- 5. Socioeconomic Environmental Studies
- 6. Scientific and Technical Assessment Reports (STAR)
- 7. Interagency Energy-Environment Research and Development
- 8. "Special" Reports
- 9. Miscellaneous Reports

This report has been assigned to the ECOLOGICALRESEARCH series This series describes research on the effects of pollution on humans, plant and animal species and materials Problems are assessed for their long- and short-term influences Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic. terrestrial, and atmospheric environments

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161

EPA-600/2-78-215 October 1978

## ASSESSMENT OF POTENTIAL TOXIC RELEASES FROM LEATHER INDUSTRY DYEING OPERATIONS

Ъy

S. B. Radding J. L. Jones W. R. Mabey D. H. Liu N. Bohonos SRI International Menlo Park, California 94025

Grant No. 804642-01-2

Project Officer

Kenneth Dostal Industrial Pollution Control Division Industrial Environmental Research Laboratory Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY CINCINNATI, OHIO 45268

# DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

#### FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs efficiently and economically.

The report briefly describes the leather tanning industry including the various sources of emissions. An attempt was made to assess the seriousness of the potential for toxic pollutant releases from the dyeing of leather. For further information on this project contact the Food and Wood Products Branch, Industrial Pollution Control Division, Industrial Environmental Research Laboratory-Cincinnati.

> David G. Stephan Director Industrial Environmental Research Laboratory Cincinnati

#### ABSTRACT

This study focused on the organic dyes released to the environment the wastewaters from leather dyeing operations. Basically, three ty dyes--acid, basic, and direct--are used, although the number of difin types of ferent dyes are well over 50, and the number of formulations used at a single tannery over the period of several years can be greater than 100. Tannery wastewaters are complex mixtures which for the most part are discharged directly into municipal sewers. The character of this di The character of this discharge will differ hourly depending on the operation performed since tanning operations are batch mode. Estimates based on information from suppliers and tanners were made of the probable discharge of dyes in The literature search revealed little or no data on the wastewater. fate of these dyes in the environment. From consideration of the physical and chemical properties of the dyes, biosorption (complexing with pro-teinaceous material) appears to be the most likely mechanism for removal of dyes in biological wastewater treatment systems.

This report was submitted in fulfillment of Grant No. R 804642-01-2 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 1 June 1977 to 28 April 1978 and was completed as of 28 April 1978.

## CONTENTS

Foreword		•	•	•				•				•			•	•		iii
Abstract		•	•	•	•			•	•	•	•					•		iv
Figures	•	•	•	•		•	•	•	•	•	•	•		•		•	•	vi
Tables .	•••	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	vii
1.	INTRO	DUU	CTIC	ON														1
2.	SUMM/	ARY	ANI	C CC	ONC	LUS	ION	S	•									2
3.	GENEF	RAL	DES	SCR	IPT	ION	OF	IN	DUS	ΓRY	•		•					4
4.	CHARA	ACTE	ERIS	STIC	CS	OF	THE	IN	DUST	ΓRY		•	•	•	•	•	•	6
	Size	and	l St	truc	ctu	re		•	•	•								6
	Envi	con	aent	tal	Im	pac	ts	•	•	•	•			•	•		•	6
	Beamh	nous	se I	Proc	es	s			•	•		•	•	•				17
	Tanho	ouse	e Pi	roce	ess	•				•		•	•	•		•	•	17
	Retar	ı, (	<b>Col</b> 0	or,	Fa	tli	quo	r P:	roce	ess	•		•	•		•		18
	Finis	shir	ng H	Proc	ces	s	•	•	•	•	•	•	•	•	•	•	•	19
	Raw N	late	eria	als		•		•	•	•	•	•	•		•	•	•	19
	Pollu	ıtar	nt S	Soui	rce	S		•	•		•	•	•	•	•	•	•	22
5.	LEATH	IER	DYI	EINC	3	•	•			•	•	•	•	•	•	•	•	31
	The I	)yei	ng	Pro	oce	ss	•	•	•	•	•	•	•	•	•	•	•	31
	Data	Acq	luis	siti	ion	•	•	•	•	•		•	•	•	•	•	•	32
	Tanne	ery	Eff	Elue	ent	Ch	arad	cte	rist	tics	s ai	nd	Trea	atm	ent	•	•	35
	Dye F	Remo	va]	l ir	n W	ast	ewat	ter	Tre	eati	nen	t	•	•	•	•	•	37
6.	TOXIC	CITY	AN AN	ID I	ENV	IRO	NMEI	NTA	L FA	ATE	OF	DY	ES	•	•	•	•	43
	Toxic	ity	of of	EDy	<i>y</i> es	•	•	•	•		•	•				•	•	43
		Тох	ici	Lty	to	Ac	luat	ic	Org	ani	sus	•	•	•		•	•	43
		Pot	ent	:ia]	L H	uma	n He	eal	th I	Effe	ect	s.	•	•	•	•	•	46
	Envir	on	ient	:a1	Fa	te	•	•	•	•	•	•	•	•	•	•	•	47
		Phy	sic	a1	Pr	оре	rtie	es	•	•	•	•	•	•	•	•	•	47
		Che	mic	al	Tr	ans	for	nat	ion	•	•	•	•	•	•	•	•	47
		Phy	sic	a1	Tr	ans	port	E	•	•	•	•	•	•	•	•	•	50
Reference	s.	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	51
A	DYES	USE	ד חי	ר א	нг	LF	∆тн	TR -	זמאז	וכידי	v							53
B.	BTODE		ר ע. דעת	יד היי	1 0.	ע ק ייי	YES		RTO	00.10	2104	ΔТ.	י. ידקד	• 4тм	• ENT	•	•	55
2.	DIODE	SYS	TEN	íS	•	•••		•	•	•	•	•	•	•	•	•		62

# FIGURES

1	Flow Diagram for Leather Tanning Process	23
2	The Uptake of Dye in Leather as a Function of pH	33
3	Effluent Treatment for a Complete Chrome Tannery	40
4	Estimates of BOD <sub>5</sub> , COD, and TOC of Effluent Streams of Tannery	41

# TABLES

1	Statistics for Leather Tanning and Finishing Industry	7
2	1976 Production Rates in Equivalent Chrome Grain Cattle Hides	8
3	1976 Production Rates in Equivalent Vegetable Tanned Cattle Hides	9
4	1976 Production Rates in Equivalent Sheep Hides	10
5	1976 Production Rates in Equivalent Split Chrome Leather Hides	11
6	1976 Production Rates in Equivalent Blue Hides	12
7	1976 Production Rates in Equivalent Retan /Finisher Hides .	13
8	1976 Production Equivalent Finished Hides	14
9	Suppliers of Chemicals to the Tanning Industry	20
10	Suppliers of Hides and Skins	21
11	Chemicals Used in Leather Processing	24
12	Estimates of Selected Chemical Usage and Losses for Leather Tanning and Finishing	28
13	Survey of the Leather Industry Tannery	34
14	Estimated Effluent Stream Load from a 1000 Cattle Hide/Day Tannery (60 lb Green Salted Cattle Hide)	36
15	Concentration of Dyes in Waste Streams	38
16	Toxicity of Acid, Basic, and Direct Dyes to the Green Alga, <u>Selenastrum Capricornutum</u>	44
17	Toxicity of Acid, Basic, and Direct Dyes to the Fathead Minnow, <u>Pimephales Promelas</u>	45
18	Photolysis of Dyes	49
19	Some Dyes Used in the Leather Industry	54

#### SECTION 1

## INTRODUCTION

describes undertaken This report a study to assess the seriousness of the potential for toxic pollutant releases from the dyeing of leather. Heretofore, most studies of pollution problems of this industry have focused on problems associated with the BOD suspended material, the high chemicals focuses only on organic and chrome in the effluent. This work dyes.

describes the As background, the report briefly industry structure; operations; the types of raw materials the processing required; the poprocess sources of emissions to air, water, the land; and tential and environmental practices. the control

#### SECTION 2

### SUMMARY AND CONCLUSIONS

This study focused on the organic dyes released to the environment in the wastewaters from leather dyeing operations. These dyes have been of concern as a health hazard to workers. A report just released by the National Institutes of Occupational Safety and Health (NIOSH, 1977) reports a striking increase in bladder cancer among both male and female leather workers, and previous studies indicate that the disease may be dye-related.

The dye types used by the leather industry include acid, basic, direct, and metallized dyes. The predominant dyes, however, are the acid and direct dyes. As many as 100 different dye formulations can be used in one plant. More than 50 dyes have been identified by eight major suppliers and from inventory lists of tanneries as used by the leather industry. Of these, 49 are listed in this report with structural formulas which indicate the wide range of materials involved.

Tannery wastewaters are complex mixtures of relatively unknown composition. Until recently, there had been no scientific assessment of the effluents, and even today, little work is being done to characterize the waste streams.

Most tanneries (90% of the tanners and 80% of the industry's wastewater) discharge their effluent streams directly into municipal sewers. The character of the waste stream depends on the particular operation being performed at that time, since tannery operations are batch mode and vary from day to day.

The chrome chemicals used in dyeing are a well-documented source of toxic materials. However, the industry has made an effort to recover or remove the chrome chemicals and many effluent streams are now low in chromium.

An extensive literature search and contacts with trade associations, tanners (4 site visits), and dye producers revealed that very little information is available (or known) on the amount of specific leather dyes released and the biodegradation of such dyes.

Even without the dyeing operation, the waste streams are highly colored, and since combinations of dyes are often used, analysis of waste streams is extremely difficult and costly.

From SRI estimates of the total dye usage by producers and tanners  $(\sim 7 \times 10^6 \text{ lbs/year or } 3.2 \times 10^6 \text{ kg/year})$  and the average uptake for dyes (60-85%), it was estimated that total leather dye releases may range from  $1.1-2.8 \times 10^6 \text{ lbs/year or } 0.5-1.3 \times 10^6 \text{ kg/year}$ . Using typical values for dye usage per hide and average wastewater flow figures, it was estimated that the actual concentration of dyes (25-50 mg/k) in a tannery

wastewater stream may be equivalent to roughly 50-100 mg/l of chemical oxygen demand (COD) out of a total raw wastewater COD of 1000 to 2000 mg/l. No useful quantitative information was obtained on the effectiveness for dye removal of wastewater treatment processes now used in the industry or by municipalities treating leather dyeing wastewaters. From a review of the literature on biodegradability of dyes, it appears that biodegradation of the dyes is unlikely to be a major mechanism for removal. It is generally assumed that performance requirements of permanent dyes is that they resist degradation under aerobic conditions; little is known about their anaerobic degradation. The biodegradation of dyes is further complicated by the batch mode of operation, which results in a wide fluctuation in the concentration of dye in the waste stream and thus may make it difficult to maintain adapted organisms for the degradation of dyes. Available data on the biodegradation of dyes have been culled mostly from the textile industry.

Removal of dyes by biosorption (perhaps by reaction with proteinaceous cellular material) may be the major mechanism for removal of dyes in activated sludge or trickling filter treatment plants. A similar mechanism may be responsible for any removal that occurs in primary clarifiers where suspended matter in the wastewater is composed of proteinaceous matter (hair and hide scraps). Dyes may thus be disposed of with the waste sludges.

The presence of proteins and chrome chemicals in tannery wastewater will most likely lead to changes in the pattern of biodegradation. Depending on the complexing, the toxicology of the dyes may also vary.

The probable fate for the general case of dyes introduced into aquatic environments is to remain in solution with sorption onto sediments and biota eventually occurring. Chemical processes or volatilization of dyes do not appear to be generally important fate processes. Long-term biodegradation probably does eventually transform most dyes, but in the absence of relevant data, such processes cannot be evaluated quantitatively.

The lack of sufficient data on the types and concentrations of dyes and the effects of other materials present in tannery effluents on the toxicology and degradation of the dyes, indicates that considerably more work will be necessary to clarify the nature and seriousness of the dye release problem from the leather tanning industry.

Future EPA research work should address the following:

- Effluent streams need to be analyzed for specific components including dyes.
- Experimental studies of the fate of dyes in various types of existing wastewater treatment systems need to be undertaken.
- An obvious approach to solution of the potential dye release problem is to segregate the wastewater streams that contain dyes and treat them separately. The technical and economic feasibility of this approach needs to be investigated.

#### SECTION 3

#### GENERAL DESCRIPTION OF INDUSTRY

The leather industry incorporates the tanners, the manufacturers of leather goods, and the suppliers of materials for both. The tanners and suppliers are limited in number, so statistics are aggregated, and much of the information is proprietary and secret, and, therefore, difficult to obtain.

It has been estimated that 25 million hides were processed in 1976, up from 22 million in 1975. Artificial leathers are not included in these numbers. The number of tanneries has steadily decreased from 7,500 in 1875 to approximately 520 establishments, including firms engaged in finishing operations on leathers tanned elsewhere.

The leather tanning and finishing industry consists of a variety of firms. Firm ownership ranges from family-owned companies and closely held corporations to divisions of large conglomerates. Information regarding operating procedures is closely held or combined with other operating information of the large corporations where segregation of data is not possible. Many of the formulations used are proprietary, and a complete breakdown as to product composition is not possible.

Most of the tanning and finishing firms are located in the Northeastern region of the country. Historically, tanneries were located near the source of hides, and it appears this may hold true for new plants. The major categories of hides used today are cattle and calfskins; sheep and lambskins; goat and kidskins; pigskins; horsehides; and deer and elk skins.

Tanners are clustered principally in the New England states, Mid-Atlantic states, Gloversville-Johnstown in New York, and the Chicago-Milwaukee area, although others are scattered throughout the country. Most of the establishments are family-owned. Tanners are classified as:

- (1) Regular tanneries
- (2) Converters

## (3) Contract tanners.

The export of hides for tanning has steadily increased, more than doubling since 1960. In 1972, over 47 percent of the hides were exported. These hides are processed to at least a salt-cured stage before shipment.

#### **SECTION 4**

### CHARACTERISTICS OF THE INDUSTRY

#### SIZEANDSTRUCTURE

Of the 517 establishments in the industry in 1972, 223 had 20 or more employees, and the industry a total 25,700 employees. had of Table 1 shows several categories of statistics the industry. on Data 1976 production of leather for the by U.S. tanneries have been compiled by states. Where fewer than three units existed in any one state. the combined (Tables 2 production rates of several states are then and 3). production in equivalent The hides of chrome grain leather of all types vegetable tanned leather utilize Table 4 and all cattle raw material. shows the production of equivalent sheep hides bv state.

A number of plants do not process the raw hides, but do split. Data on these are given in chrome tan. retan, and/or finish the hides. Tables 5, 6, 7, and 8. These operations should not be counted in the production, since this would result total in double counting.

#### Environmental Impacts

#### Processing Operations

There are four steps in processing hides: beamhouse: tanhouse: process color, and fatliquor; and finishing. The beamhouse retan. is sheepskins or tanning and finishing, and the other not used in pigskin processes will vary somewhat. For example, the fleshing step. which is carried performed the beamhouse process for cattlehides, is out in in sheepskins. Sheepskins process for not always dehaired, the tanhouse are but they are degreased. Essentially the processing follows the steps outlined below.

#### Beamhouse Process

Receiving -Nearly all cattlehides received at tanneries are (1)either cured brined hides. with brined green salted or hides predominating. In few isolated cases where transit time is а

<sup>\*</sup> Source: "Development Document for Effluent Limitations Guidelines and Source Performance Standards for Leather Tanning Finishing," New and EPA-440/1-74-016a, 1974. March

						- )			
No.	of								
<u>establi</u>	shments	rol		•			<del>.</del> :		₩21 of
	With 2	0		Produ	ction wo	rkers	Value	COST OI	Value UL
	employ	r- A11	employees		Man-		added by	materials,	industry
	ees or	: Number	Payrol1	Number	hours	Wages	manufacture 6	fuels, etc.	shipments
Total	more	(10 <sup>7</sup> )	(\$10 <sup>0</sup> )	( <sub>201</sub> )	$(10^{0})$	(\$10 <sup>0</sup> )	(\$10 <sup>0</sup> )	(\$10^)	(\$10~)
517	223	25.7	200.0	22.1	41.9	\$151 <b>.</b> 3	\$368 <b>.</b> 3	\$708 <b>.</b> 0	\$1 <b>,</b> 059.5
Source:	U.S.	Department	: of Commerc	e, Census	of Manu	facturers,	1972.		

`

TABLE 1. STATISTICS FOR LEATHER TANNING AND FINISHING INDUSTRY (1972)

7

	No. of	
States	plants	Production
California	7	1,404,114
Tennessee	6	821,516
Wisconsin	12	3,959,529
Illinois	6	772,757
Michigan	3	1,449,183
Pennsylvania	4	733,627
Massachusetts	11	1,706,850
New York	12	1,317,530
New Jersey	4	577,251
Maine	5	2,023,458
New Hampshire	4	1,080,291
Oregon	3	95,000
Alaska Washington Colorado	$\begin{pmatrix} 1\\2\\2 \end{pmatrix}$	64,000
Utah Minnesota Nebraska Missouri	$ \begin{array}{c} 1\\2\\1\\2 \end{array} $	1,015,638
Louisiana Florida Virginia	$\begin{pmatrix} 1\\2\\1 \end{pmatrix}$	33,152
Delaware Ohio Vermont Maryland	$ \begin{array}{c}1\\1\\1\\1\end{array}\right\} $	437,386
TOTAL		17,491,282

TABLE 2. 1976 PRODUCTION RATES IN EQUIVALENT CHROME GRAIN CATTLE HIDES\*

\* One equivalent hide  $\simeq 40$  ft<sup>2</sup> of leather (3.72 sq.m). Source: Tanners' Council of America, Inc., 1977.

No. of Plants	Production
3	490,750
4	925,043
$\begin{pmatrix} 2\\1 \end{pmatrix}$	101,841
$\left.\begin{array}{c}1\\1\\2\end{array}\right\}$	1,000,271
1 2 1 1	535,371
	3,053,276
	No. of Plants 3 4 2 1 1 1 2 1 1 2 1 1 2 1 1 1 1

# TABLE 3. 1976 PRODUCTION RATES IN EQUIVALENT VEGETABLE TANNED CATTLE HIDES\*

\* One equivalent hide  $\simeq 40$  ft<sup>2</sup> leather (3.72 sq.m). Source: Tanners' Council of America, Inc., 1977.

	No. of	
<u>States</u>	<b>plants</b>	Production
Massachusetts	13	850 <b>,</b> 592
New York	16	1,140,544
New Hampshire	4	416,044
Maine	4	383,677
Colorado New Jersey Texas Pennsylvania Florida Wisconsin	1 1 1 2 1 1	147,429
TOTAL		2,939,286

# TABLE 4. 1976 PRODUCTION RATES IN EQUIVALENT SHEEP HIDES

\* One equivalent hide  $\simeq 40$  ft<sup>2</sup> leather (3.72 sq.m). Source: Tanners' Council of America, Inc., 1977.

Statos	No. of	D. 1
States	plants	Production
Massachusetts	13	1,218,183
Wisconsin	5	1,394,605
California Illinois New Hamshire	$\begin{pmatrix} 1\\1\\1 \end{pmatrix}$	957,827
TOTAL		3,570,615

TABLE 5. 1976 PRODUCTION RATES IN EQUIVALENT SPLIT CHROME LEATHER HIDES\*

\* One equivalent hide  $\simeq 40$  ft<sup>2</sup> leather (3.72 sq.m). Source: Tanners' Council of America, Inc., 1977.

States Colorado	No. of plantsl	Production
Arızona Iowa Minnesota Missouri New Jersey Massachusetts	1 2 1 1 1 1	2,181,000
TOTAL	_	2,181,000

TABLE 6. 1976 PRODUCTION RATES IN EQUIVALENT BLUE HIDES\*<sup>†</sup>

\* One equivalent hide  $\simeq 40$  ft<sup>2</sup> leather (3.72 sq.m) † "Blue" usually is applied to hides or skins

that have been chrome-tanned but not dyed or fat-liquored.

Source: Tanners' Council of America, Inc., 1977.

	No. of	
States	plants	Production
Pennsylvania	3	95,000
Massachusetts	6	720,000
New York	3	255,000
New Jersey	3	80,000
California Tennessee Wisconsin	$\left.\begin{array}{c}2\\1\\1\end{array}\right\}$	731,254
TOTAL		1,881,254

# TABLE 7. 1976 PRODUCTION RATES IN EQUIVALENT RETAN/FINISHER HIDES\*<sup>†</sup>

\* One equivalent hide  $\simeq 40 \text{ ft}^2$  leather (3/72 sq.m)

Retan/finishers perform only the last retan and finishing operations. The raw materials for these operations are the chrome or vegetable tanned hides.

Source: Tanners' Council of America, Inc., 1977.

	No. of	
<u>States</u>	plants	Production
Massachusetts	22	2,550,000
New York	12	1,075,000
New Jersey	10	482 <b>,</b> 356
Ohio	3	57,981
California Tennessee Delaware North Carolina New Hampshire Wisconsin	$   \begin{bmatrix}     1 \\     1 \\     2 \\     1 \\     1 \\     1   \end{bmatrix} $	615,000
TOTAL		4,780,337

# TABLE 8. 1976 PRODUCTION EQUIVALENT FINISHED HIDES\* †

\* One equivalent hide  $\simeq 40$  ft<sup>2</sup> leather (3.72 sq.m).

† Finishers work only on the surface of tanned grain or split leather to give a uniform finish to the leather.

Source: Tanners' Council of America, Inc., 1977.

green hides without prior curing have been sent dishort, rectly from a packer to a tannery and processed. Green hides. after trimming and grading, are cured at the packing house by spreading the hides, flesh side up, and covering them with salt. This process continues until a pack of hides about 5 to 6 feet high is obtained. A heavy layer of salt is placed over the top hides. The natural liquid of hides dissolve a layer the of portion of the salt to form a brine. In this process, salt is absorbed and. bv diffusion and osmosis. causes а reduction of the moisture content in the hide. After 10 to 30 days from the date the pack is closed, the hides are considered adequately cured. Each hide is shaken to get rid of excess salt and is either to folded individually; the hides are shipped in packs, tanneries or to warehouses for storage. The size of the pack depends on a number of variables, such as size of the packing house, size of shipments, and the method of shipment. Brined hides are prepared at the packing house or at a separate hide processing facility by agitating fresh hides in a saturated replaced solution salt has desired amount brine until the the of moisture within the hide. In this process, hides are also attached foreign matter. cleaned by removal of manure and other Hides are then removed, drained, and bundled in a manner similar to that used for green salted hides. Hides may be fleshed before or after brining. "Safety salt" is usually sprinkled shipment. The brining process takes on each hide before two three days, which makes it attractive to the packer or hide to establishment, since there is no need to hold a large curing hides. The brining process is preferred by inventory of most tanners and packers since it tends to produce cleaner hides.

- (2)Storage - Hides are normally stored at the tannery in the pack as received. No special storage conditions are maintained in other than that required to keep hides most tanneries at the moisture content as received.
- Siding and Trimming The usual first step in the processing (3)of hides from storage at the tanner is to open a folded hide and trim it. The hides then may be cut in half along the backto as halving or siding. Sometimes which is referred bone. hides are halved after unhairing or tanning.

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

- (4) Washing and Soaking - Sides (or in some cases whole hides) siding and trimming operation are placed in vats from the (with or without paddles), drums, or hide processors (conmixers with special linings) for washing crete and soaking restore moisture. Water usage to is generally less with hide processors, although some tannery people have expressed the opinion that equivalent reduction in water can be use achieved with drums. This process removes dirt. salt, blood. nonfibrous proteins manure. and from the hides. The quansuch waste material varies, depending the time tity of on of year and the source of the hides. Depending on the type of leather produced, additional washes (rinses) may also several other points tanning process, inoccur at in the cluding after and dehairing, after bating, liming after tanfollowing ning. and prior to and coloring.
- Fleshing -Fleshing is the removal of attached adipose fatty (5) tissue and meat that have been left on the hide at the pack-It is done on a fleshing machine, in which the ing house. hide is carried through rolls and across rotating spiral blades that remove the flesh from the hide. Cold water is necessary to keep the fat congealed, but the fat represents additional an waste disposal load. Most hides are fleshed at the packing house or at a separate hide processing faof brined hides. cility, particularly in the case When flesh is removed prior to liming it is referred to as green fleshwhen it is performed after liming it is referred to as ing; lime fleshing. In any case, fleshings are normally recovered and sold to plants for rendering or conversion to glue. If fleshings properly handled, there is very little are liquid solid waste contribution from operation. or this
- Unhairing Hair is removed by chemical loosening followed (6) bv either machine pulling or chemical dissolution of the Machine removal is practiced when the processor dehair. dissolving process is referred to recover the The sires hair. as "pulping" or "burning." to

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

pulped, stronger solutions and/or longer time cycles are used and the hair may be totally dissolved.

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

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

#### Tanhouse Process

- Bating -Bating is the first step in preparing the stock for (1)the tanning process. It may be done in either vats (with or without paddles), drums, or hide processors. The hides are placed in the processing equipment, which contains а solution ammonium salts and enzymes. The purpose of this operation of is to:
  - a. De-lime skins.
  - b. Reduce swelling.
  - c. Peptize fibers.
  - d. Remove protein degradation products.
- Pickling pickling subprocess follows the bating The step (2)is normally in the same equipment. and done A brine and an acid solution is used bring the hides condition to to an acid preparation subsequent addiin for tanning subprocesses. In conditioning hide receiving tanning tion to the for the agent, this step prevents precipitation of chromium salts. Pickling is always done before the chrome tanning process and may be done before vegetable tanning.
- Nearly all cattlehides Tanning in this country are either (3) vegetable tanned; little is chrome or very tanned with alum tanning or other materials.

tanning is performed Vegetable the older process, and is in solution containing plant extracts such vegetable tanа as method is usually the heavy nings. This used for leathers

mechanical leathers. saddle leathers. such as sole leather. and are Shoe upper leathers and other lighter leathers usually chrome tanned by immersion in а bath containing proprietary of mixtures basic chromium sulfate.

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

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

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

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

### Retan, Color, Fatliquor Process

- (1)Retan - Retanning is done principally different to impart characteristics in finished leather the that would be lacking if tanning were carried out in one step. Retanning may use chrome, vegetable, synthetic tanning agents, it is or and usually done in drums immediately preceding coloring and fatliquoring.
- (2) Bleaching – Bleaching hides with sodium bicarbonate and sulfuric acid after tanning is commonly practiced in the sole leather industry. Bleaching is done in vats drums. or
- Coloring Coloring is done in the same drums (3) as retanning, may be before or done either and after fatliquoring. Natural dyes may be used, but many synthetic products are now available for this purpose.

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

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

#### Finishing Process

Finishing operations such as drying, wet-in coating, staking or tacking, and plating, which follow the wet processes, provide only minor contributions to the liquid waste. These result primarily from cleanup of the paster drying plates and from paint spray booth water baths. Trimmings are disposed as solid waste, and dust collected may be disposed in either wet or dry form.

## Raw Materials

The production of synthetic tanning materials alone in 1974 was estimated by the U.S. International Trade Commission at 60,570,000 pounds (27,531, 818 kg) for a total value of \$16,031,000. Table 9 lists some of the manufacturers of these materials.

Many of the products used in tanning and dyeing are proprietary formulations and a complete breakdown as to product composition is not possible.

Allied Chemical Corp. American Cyanamid Co. Atlas Refinery, Inc. Barkey International Corp. BASF Wyandotte Corp., Carlstadt Leather Fin. Birko Chemical Corp. Chemical Coating Materials Co. Ciba-Geigy Corporation Eastern Industrial Oil Prod. Co., Div. of Henkel, Inc. Industrial Chemical Co. Kepec Chemical Co. Kepec Div. of Hendel, Inc. L. H. Lincoln & Son, Inc. Marden-Wild Corporation Diamond Shamrock, Napco Chemical Div. A. J. & J. O. Pilar, Inc. Pilar River Plate Corp. PPG Industries, Inc. Prime Leather Finishers Co. K. J. Quinn & Co., Inc. Rohm & Haas Company Salem Oil & Grease Co. Sandoz Colors & Chemicals Samuel Smidt Chemical Corp. Stahl Finish - Beatrice Chem. Div. of Beatrice Foods Co.

Staley Chemical Division Tac Tannins & Chemicals, Inc. Arthur C. Trask Corp. Union Carbide Corp. Verona Dyestuff Div., Mobay Chem. Corp. Wayne Chemical Corp. Weber & Smith, Inc. Whittemore-Wright Co., Inc. Eric C. Baum Assoc., Inc. Hamblet & Hayes Co. The Hine Line Hooker Chemicals & Plastics Corp. Industrial Commodity Corporation International Advisory Service Johnson & Carlson Korium Associates, Inc. Norton Co. Quaker City Hide Co. Redi-Stac, Inc. The Roit Corporation Chas. H. Stehling Co. Arthur C. Trask Corp. USM Corp-Turner Tanning Machinery Div. Woburn Machine Co.

Source: Tanners' Council of America Directory, "Leather and Suppliers to the Tanning Industry," July 1975. Suppliers of hides and skins are listed in Table 10. The hides are usually cured green salted or brined by the supplier unless transit time is very short.

Andrews Hides, Inc.	The S. J. Kibler & Bros. Co.
M. Aschheim Co., Inc.	M. Lyon & Co.
G. Bernd Company	A. Mindel & Son, Inc.
Booth Agencies (Boston), Inc.	Muskegon Hide Company
Harold Braun & Co., Inc.	Packerland Packing Co., Inc.
Harold M. Brodsky, Inc.	Philadelphia Hide
Cahen Trading Co., Inc.	Brokerage Corp.
George P. Cavanaugh, Inc.	B. N. Ritter & Co.
Chilewich Corp.	Rockford Hide Co.
Herbert A. Cohen Co.,	St. Louis Hide Co.
Denison Hide Co., Inc.	Frank J. Schwab
Dietrich Hide Corporation	Associates, Inc.
Eden & Strass, Inc.	Sklut Hide & Fur Co.
H. Elkan & Company, Mass.	Southern Tier Hide & Tallow, Inc.
H. Elkan & Co., I <b>11</b> .	Southwestern Trading Company
George H. Elliott Company	Spencer Foods, Inc.
Estra Trading Company	Swift Fresh Meats Co Hide Division
Evansville Technical Corp.	Transcontinental Industrial Co., Inc.
Paul Gallagher & Co., Inc.	Union Hide Company, Inc.
Fred Gruen Co., Inc.	A. L. Webster Co.
Hickman & Clark, Inc.	WeCo
Hide Service, Inc.	Western Hide Co., Inc.
J. C. Hodges & Co., Inc.	G. A. Wintzer & Son Co.
A. J. Hollander & Co., Inc.	
Kaufmann Trading Corp.	

TABLE 10. SUPPLIERS OF HIDES AND SKINS

Source: Tanners' Council of America Directory, "Leather and Suppliers to the Tanning Industry," July 1975.

Cattlehides constitute the major portion of tanning in the United States and are estimated to represent 90% of the total. Sheep and lamb, followed by pigskin, are the next largest categories, constituting less than 10%. A very small amount of other hides tanned include exotic hides such as shark, seal, kangaroo, elk, and moose.

A flow diagram for the tanning processes is given in Figure 1. The chemicals used in the processing techniques are outlined in Table 11. A new process had been proposed (Chem. and Eng. News, 1974) by USDA to replace the controversial salt curing of the hides. USDA claims this not only reduces pollution but also produces quality process leather at a lower cost. Cyanides have eliminated according to industry also been sources. and the use of trichloroethylene is decreasing. The chemicals used in tanning listed on the EPA toxic substances list are enclosed in boxes in Table 11 wherever they can be identified. In each step of tanthe potential exists for both water and solid wastes. Materials ning, that can appear in tannery wastes are listed below:

Hair		Salts
Hide scra	ps	Tanning
Flesh		Soda ash
Blood		Sugars and starches
Manure		Oils
Dirt		Fats
Salt		Grease
Lime		Surfactants
Soluble	proteins	Mineral acids
Sulfides		Dyes
Amines		Solvents
Chromium		

Because of the nature of the industry, breakdown of figures for total sales of tanning materials and dyes cannot be obtained without revealing information on individual companies. Estimates of chrome chemical and dyes usage have been made and are shown in Table 12. Estimates of dye consumption by the leather tanning industry differ greatly depending on the source. Dye manufacturers estimate the market at from 3 to 7 x 106 lb dye/yr (1.36 to 3.18 x 106 kg/yr); the calculation based on data from tanning industry representatives indicates use could be as high as 30 x 10<sup>6</sup> lb dye/yr (13.6 x 106 kg) . However, it is felt that an estimate of 7 x 10<sup>6</sup> lb (3.18 x 106 kg) annually is more realistic based on the number of hides dyed and the average dye loading to the dyeing operation.

### Pollutant Sources

The will operating parameters (e.g., concentration,temperature) vary from tanner to tanner, and since much of the information on formupotential loading and composition of waste lations is proprietary, the difficult streams is to assess.





		Disinfectants	1
	Ĺ	Nonionic surfactants	Alkanol ethoxylate
	Soaking	Soda ash (sodium carbonate)	Alkylphenyl ethoxylate
		Sodium polysulfide (tetra)	j
		Sodium sulfide	
		Calcium chloride	Sodium sulfides Sodium hydrosulfide
		Sharpening agents	Sodium sulfite
	Liming	Lime	Amines Dimethylamine sulfate
	(Unhairing)	Proteolytic enzymes	Cyanides
		Nonionic surfactants	
			<u>Alkylphenyl</u> ethoxylate
		Ammonium sulfate	
		Ammonium chloride	
Doctodaroo	Dotino	Formic acid and salts	Sodium formate
Process	Dating	Proteolytic enzymes	Oropon bates (Rohm & Haas Co.)
		Nonionic surfactants	
		1	Alky1pheny1 ethoxy1ate
	Deoreasino	Sheepskin and pigskin	Kerosene
	2-9117020	degreased after bating	Stoddard solvent
		J	Nonionic surfactantAlkanol ethoxylate
			Soaps
			Anionic surfactants Sulfated oils and alkyl sulfates
			Alkyl benzene sulfonates
			Triethane (Trichlor-
			ethylene and perchlor-
			ethylene)
	Pickling	Sodium chloride Sulfuric acid	

TABLE 11 (Continued)



TABLE 11 (Continued)


o of acrylic copolymers - Primal Emulsions (e.g.) nic surfactants		<pre>chloride complex of perfluro fatty acids ocarbons</pre>	Alcohols Polyols Glycol - ethers Esters and ethers Ketones	White - titanium dioxide White - titanium dioxide Black - carbon black, bone black, iron oxide Yellow - lead chromate, cadmium sulfide-selenides, iron oxide Orange - lead chromate	Brown - iron oxide Blue - phthalocyanin blue, iron blue, ultra-marine blue Green - phthalocyanin green, chrome green Red - cadmium sulfide-selenide, organic lakes and toners
Impregnation Aqueous emulsions	Patent Naphtha leathers Boiled linseed oi	Water or oil Stearato chromic Chrome complexes repellent Chlorinated hydro	Ing Solvents for Oils	Nitrocellulose lacquers	Figments in water solution concerns some hardening protein such as shellac or albumin
			Finish: Proces		

-----

Note: Orthodichlorobenzene is recommended for masking odors of decaying flesh. Paradichlorobenzene is used for controlling parasites and mothproofing wool on sheepskins.

Source: SRI International.

#### TABLE 12. ESTIMATES OF SELECTED CHEMICAL USAGE AND LOSSES FOR LEATHER TANNING AND FINISHING

Chrome Chemicals (Source: Dr. Robert Lollar of the Tanners' Council of America, Inc.)  
Basis: One equivalent hide ~ 40 ft<sup>2</sup> of leather (3.72 sq.m).  
~ 25 x 10<sup>6</sup> hides to be tanned in 1976  
(~ 22 x 10<sup>6</sup> hides tanned in 1975)  

$$\left(\frac{25 \times 10^6 \text{ hides}}{\text{year}}\right)\left(\frac{50 \text{ lb}}{\text{hide}}\right) = \frac{1.25 \times 10^9 \text{ lb}}{\text{year}}$$
  
 $\left(\frac{0.35 \text{ lb collagen}}{\text{ lb}}\right)\left(\frac{1.25 \times 10^9 \text{ lb}}{\text{hide}}\right) = \frac{385 \times 10^6 \text{ lb collagen}}{\text{year}}$   
 $\left(\frac{0.06 \text{ lb chrome oxide fixed}}{\text{lb collagen}}\right)\left(\frac{385 \times 10^6 \text{ lb collagen}}{\text{year}}\right) = \frac{22 \times 10^6 \text{ lb chrome oxide fixed}}{\text{year}}$   
 $\frac{23 \times 10^6 \text{ lb chrome oxide/year}}{(0.7 \text{ of total used is fixed})} = \frac{33 \times 10^6 \text{ lb chrome oxide required}}{\text{year}}$ 

Dyes (Calculated by two different methods)

- Based on estimated dollar value of dye market (Source: Personal communication with representative of dye manufacturers)
  - Basis: Value of dyes sold ≈ 15 x 10<sup>6</sup>/year Average price of \$3/1b (6.60/kg) Consumption range 5 x 10<sup>6</sup> 1b/year Estimated sales distribution Acid dyes \$9 million Direct dyes \$3.7 million Basic dyes \$1 million Solvent dyes \$1 million
- B. Based on production figures for leather and average dye used. (Source: Personal communications with representatives of tanneries)
  - Basis: Percent of dye used ranges from 0.25-2% for most operations. Industry sources suggest 0.7% as an average of dye used per pound of hides; approximately 80% of all hides are colored.

Therefore:

$$\left(\frac{20 \times 10^6 \text{ hides}}{\text{year}}\right) \left(\frac{50 \text{ 1b}}{\text{hide}}\right) (0.007) = 7 \times 10^6 \text{ 1b dye/yr used (3.18 x 10^6 kg/yr)}$$

Dye loss to sewer may range from 1.1 to 2.8 x  $10^6$  lb/yr for the industry (0.5 to 1.27 kg/yr).

\* Fraction of leather that is chrome tanned.

Source: See individual sources listed in table.

Waste streams are identified below as liquid or solid, according to the unit operation of each process. Air pollution is limited to odor problems.

		Waste Pr	oduct
	Unit Operation	Liquid	Solid
Beamhouse Process	Siding and trimming	х	х
	Washing & soaking	х	Х
	Fleshing	х	Х
	Unhairing	Х	Х
Tanhouse Process	Bating	X	
	Pickling	X	
	Tanning	X	Х
	Splitting		
Retan, Color, Fat-	Retan	х	x
liquor Process	Bleaching	х	
114001 1100000	Coloring	х	x
	Fatliquoring	X	
Finishing Process	Drying, wet-in coating tacking,	х	x

### Waste Streams

Materials that can appear in tannery wastes include the following:

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

In the beamhouse process, dirt, salt, blood, manure and nonfibrous proteins are removed from the hides. Depending on the time of the year and the source of the hides, there is considerable variation in the quantity of such wastes, and additional rinses may be necessary at several points in the beamhouse process, depending on the type of leather produced. Fleshings, if properly handled, produce little solid or liquid wastes. However, the liming and unhairing steps are principal sources of waste effluent. A save-hair operation substantially lowers the waste effluent. The tanning process generates substantial wastes. While recycling of tanning solutions is becoming more common, there is still considerable waste. Evaporation and recovery is possible, and the waste solutions can be used in retanning. Liquid wastes from the retan, color, and fatliquor process may be high volume-low strength in comparison to the other processes. The finishing process generates trimmings as solid wastes, and dust in either wet or dry form. The other steps in finishing contribute only minor amounts to the liquid waste streams.

### SECTION 5

## LEATHER DYEING

### THE DYEING PROCESS

carried out on chrome or Leather dveing is blue hides. These are that have been through dehairing, washing, soaking, fleshing, hides bating, and either a chrome,alum, or vegetable tanning. Generally, dyeperformed in a batch mode and retan, coloring and fatliquoring ing is operations are all performed in sequence in the same drum without intermediate steps of washing and drying.

Hides the blue in drums and retan at stage are placed formulations appropriate designated dye formulation is added added; at the time, a are mixing rotation) Fatliquoring chemicals added and (by is continued. are at the prescribed time. Cycle times for this sequence can be as high as 8 hours .

Three of dyes are used: acid. basic. and direct. Acid major types with are usually azo, triarylmethane, anthraquinone dyes acid dyes or substituents such nitro-, carboxy-, sulfonic acid. Basic dyes as or contain free amino groups. Direct dyes are principally water-soluble salts dyes. of sulfonic acids of azo All the dyes used by tanning industry the are sufficiently water-soluble and have an affinity for leather; they are Both acid basic dyes the proper pH values protein-binding dyes. and at dyes deeper hide; direct are not penetrating when penetrate into the used the blue vegetable tanned leather. Acid dyes are fixed more readily on or at low pH. but penetrate deeper as the pН increases. Basic dyes, as the name implies, are fixed at high pH values. However, basic dyes have to used with a vegetable tanning material anionic syntan to dve be or an chrome leather. uptake of is a function of Thus, the dye in the leather syntans the float. float levels the dye used, pH, present, and High liquor hides) may to maintain (ratio of to be necessary even coloring. The end use of the leather also determines how deep the color needs to leather. For upholstery for is suitable bebe. example, surface dyeing cause of the light use. For shoe or garment leather, deeper penetration Blends of dyes of the dye is required. are used in order to obtain the exact shade desired.

The relationship between pH and uptake of dye is shown in Figure 2. Thus, in practice, pH adjustments may be made to assure penetration and fixing of an acid dye, while a basic dye may be added at a later point in the dyeing process to coprecipitate with the acid dye.

After the dyeing process, the liquid is drained off, the leather is pressed, and all the effluent is disposed of at one time.

### DATA ACQUISITION

extensive collect information An literature search was made to on dyeing of leather. but this resulted in little data. Therefore, on-site visits deemed tanneries. which were necessary. Visits were made to four were chosen from a list recommended by the National Tanners' Council. Topics for discussion were as follows:

- Number of formulations used in dyeing.
- Colors (range, predominant colors)
- Types of dyes
- Loading
- Float
- Dye/1b of leather
- Dye lost/lb of leather
- Cycle times
- Effluent characteristics.

The results of the survey are given in Table 13. Suppliers were also contacted to determine which dyes are used by the leather industry. formulations From all sources. it is apparent that dye are trade secrets or handed down in family-owned businesses. In many cases, suppliers prepare the formulation to meet a specific color demand for one of the tannery's clients, and the tannery has no knowledge of the exact nature of this formulation. All colors are made up on demand and several different colors may be used in any one day.

The quantity dye used depends on the of color, the type of leather or grain, cattle, sheep, or other), and even the mix of dyes. (split, specific Mixtures of dyes are often used to obtain а color. The uptake of dye by the leather also depends on the color desired. Cycle times are from 4 to 8 only estimates are available on actual hours and dye



SOURCE: Thorstensen, T.C., Practical Leather Technology (R.E. Krieger Publishing Co., Huntington, New York, 1976), p. 178.

SA-5619-21

FIGURE 2 THE UPTAKE OF DYE IN LEATHER AS A FUNCTION OF pH The acid dyes fix more at low pH. The reverse is true of the basic dyes. A direct dye has high fixation over a wide pH range.

			Tannery	
	A	В	υ	D
No. of formulations used in dyeing	300, 50 active (some spray dyed)	15 (all mill dyes)	60-65	50-70
Colors (Range, predominant colors)	Brown, black, cream white and others‡	Yellow, white, natural*†	Mostly browns, black, but some of all other colors	Mostly browns, black, but some of all other colors
Types of dyes	Direct, acid, basic, metallized	Direct, acid (50/50)	Acid, direct, metallized	Acid, direct, metallized
Loading (typical or aver- age range) Float Dye/kg of leather (wet)	2-3/1 Δ	~4/1 typical 6 kg/900 kg or 0.7%	1-2/1 0.25 - 5%	1-2/1 0.25 - 2%
Dye lost/kg of leather	Unknown,estimate 50 to 80% dye uptake	Unknown, estimate ~90% uptake on av.	Estimate uptake >95% on lighter dyes	Estimate > 90% to 95% uptake on most colors except chocolate browns
Cycle times	4 to 8 hr	4.5 - 5 hr	4-9 hr (av. = 7.5 hr)	4 to 8 hrs
Effluent characteristics	0.4 mgd	~l mgd total to municipal sewer	No data - directly to municipal sewer	20 to 40 BOD except when $t < 20^{\circ}$ F; then BOD can go up to 200 under severe winter conditions
Products	Garment & shoe leather	Chrome tanned up- holstery leather	Garment & shoe leather	Shoe leather mainly
Production (average)	~ 1000 hides/day	10,000 actual hides/ week	\$	3250 hides/day
Source of hides	90% glove chrome- tanned, full grain cattle hide, some deer, elk, sheep, goat	Cattle	Cattle	Cattle, beef

TABLE 13. SURVEY OF THE LEATHER INDUSTRY TANNERY

? = unknown . \* ~ 50% of output is not dyed--natural color develops during retan and fatliquoring. † \$ 10% of production is dyed a variety of red, green or blue colors. ‡ Violets, blues, greens, purples. △ Tan 0.25 to 0.5%, light brown 0.25 - 0.5%, med. brown 0.5 - 0.75%, dark brown 1 - 2%.

uptake. Splits take up more dye and therefore more dye is added to the batch. Estimates of uptake range from 60-95%.

## TANNERY EFFLUENT CHARACTERISTICS AND TREATMENT

No data were obtained from the literature or from individual tanners on the content of dye in the raw or treated wastewater. The literature reports that effluents from tanneries are colored, but it has not been verified that this results solely or in part from dyes.

Currently, wastewater from about 90% of the tanners, accounting for approximately 80% of tannery industry production, is discharged to municipal systems. The estimated flow from a 1,000 hide/day cattle hide tannery (basis: 60 lb/salted hide) based on an average of 12 tanneries (from a study by Thorstensen Laboratory) is 1.61 x  $10^6 \ l/day$  (~ 58.2 l/kgof salted hide or 70.8 l/kg of hide). A study for the EPA (1974) is based on several different volumes, of which an average of 1.14 x  $10^6 \ l/day$ appears to us to be the best estimate for a 1000 hide/day tannery.

A breakdown of effluent loadings from the different operations (Table 14) shows a variation of BOD from 22.7 to 1364 kg/day and total suspended solids of 81.8 to 1773 kg/day. The total flow rate may vary considerably among tanneries, and the color of the effluent will vary from light yellow-orange to a brown color.

Effluent treatment varies with the relationship of the tannery and its community. A small tannery's discharge in the sewer of a large community may be hardly noticeable, whereas a large tannery in a smaller community would have a greater impact. Also, tanning operations are not continuous but are on a batch basis. Thus, effluent composition is likely to be quite variable if there is no equalization or holding basin.

The treatment of effluent generally follows several steps: screening, coagulation, settling, and in some cases, an activated sludge operation. For the four tanneries visited, little was known of the exact chemical characteristics of the effluent, and efforts are only recently being made by EPA contractors to identify specific compounds or constituents.

Tanneries are approaching the water pollution abatement problem in different ways. On-site activiated sludge plants have been installed in some cases and are completely owned and operated by the tannery. In other instances, the activated sludge operation is set-up and controlled by the tannery only until it is operational, after which it is turned over to the city. In most instances, waste streams are still fed directly into

			Total					
			suspended	Total	011 and			
Processing	Flow /10 <sup>3</sup> //daw)	BOD	solids (Veldav)	solids (Volday)	grease (to/day)	Sulfide (bo/day)	Chromlum /be/dav/	Нч
0 4 5 9 5	1 A A A A A A A A A A A A A A A A A A A	VXV/ nall	VEN 1911	VvR/ naj /	1481 uay 1	1487.447.1	148/ 447 /	
Soaking	189	409	682	5,864	1	ŀ	:	6.0-8.0
Unhairing	189	1,364	1,773	4,090	273	205	1	11.0-12.5
Liming	379	273	409	1,364	136	273	;	11.0-12.5
Bating	227	22.7	161	545	545	:	;	7.0-10.0
Chrome tanning	57	10.9	136	4,090	273	t 3	136	3.5-4.0
Retan, coloring and fatliquoring	379	54.5	81.8	545	45 <b>.5</b>	:	27.3	4.0-5.0
Finishing	189	81.8	136	218	273	:	:	5.0-8.0

UTDE/DAV TANNEBV Þ State V A 1000 ŝ 0 TADTO 1/

·

36

the municipal system without prior treatment. Because the effluent streams can be highly colored even in the absence of dye, the tanneries have been unable to estimate the actual amount of dye in the stream.

Based on estimates available of the dye consumed (see Table 13) and a water usage of  $1.14 \ge 10^6 \ l/day$ , calculations were made of the concentration of dye in (1) effluent streams of the entire plant operation at high, average, and low water usage, and (2) the dyeing operation effluent stream only. These are shown in Table 15.

#### DYE REMOVAL IN WASTEWATER TREATMENT

Our search of the literature and discussions with selected industry representatives did not result in useful information on dye removal in wastewater treatment. However, some extrapolation of the data is possible, as described below.

A past EPA study (Thackston, 1973) reported that ". . . color in the spent dye wastes was not removed or diminished by biological waste treatment." The dyes used at the tannery under study were mostly acid dyes. Some dye solution reuse was being practiced during the EPA test program, but is not being done now. The current operations include almost all alum tanning and the activated sludge plant effluent is a "bourbon color" (Caldwell Lace, 1977). Mostly brown dyes are used at the tannery, although some orange dyes are used from time to time.

Figure 3 shows hypothetical stream compositions based on some typical data from the literature and estimates of dye concentrations. A value of 2 mg COD/mg dye has been calculated for a widely used dye. As shown in Figure 3, the dyes would represent less than 2% of the COD of the raw wastewater to primary treatment. It is difficult to predict, however, how much of the soluble COD is contributed by the dyes or what fraction of the dye is in solution or sorbed on suspended matter.

In the previously mentioned EPA tannery study, if it is assumed that the reported dye use is typical of the industry, the dye would be expected to contribute from ~ 44 to 112 mg/liter of COD or 11 to 28 mg/liter of TOC. Results of COD and TOC measurements of filtered samples of raw waste influent to the treatment plant, primary effluent, and secondary effluent are plotted in Figure 4 along with BOD<sub>5</sub> measurements of unfiltered samples. Much of the BOD<sub>5</sub> was attributed to high suspended solids levels in all three sampling points. The data show that soluble organics removal is quite good and that the soluble COD level and TOC levels possibly contributed by the dyes are low relative to the raw

#### Float Ratio and Percent Dye Use

We can calculate the volume of dye waste streams and dye concentrations as follows:

Average water use per hide in dyeing (float of 2/1; 50#/hide		2000 lb water/ 100 lb hides
Average dve used per hide	Ħ	2
(0.7% of a 50# hide)	=	0.35 lb

Range of Uptake

Dye Required

$$\left(\frac{20 \times 10^6 \text{ hides}}{\text{yr}}\right) \left(\frac{50 \text{ lb}}{\text{hide}}\right) \left(0.007\right) = 7.00 \times 10^6 \text{ lb dye} \text{ required/yr}$$

Upper Limit of Dye Fixed

(Dye required, 1b)   

$$\begin{cases}
\text{Uptake of 75\% for 10\% of hides} \\
\text{Uptake of 85\% for 90\% of hides} \\
\text{Uptake of 85\% for 90\% of hides}
\end{cases}$$
Range of dye fixed at upper limit
  
 $(7.00 \times 10^{6})(0.75)(0.10) = 0.53 \times 10^{6}$ 
  
 $(7.00 \times 10^{6})(0.85)(0.90) = 5.36 \times 10^{6}$  1b
  
 $= 5.89 \times 10^{6}$  1b fixed total

.

Lower Limit of Dye Fixed  $(7.00 \times 10^6)$  (0.60) = 4.2 x 10<sup>6</sup> lb fixed Dye Loss Range =  $(7.00 \times 10^6 - 5.89 \times 10^6)$  to  $(7.00 \times 10^6 - 4.2 \times 10^6)$ = 1.1 x  $10^6$  to 2.8 x  $10^6$  1b dye

Overall Industry Wastewater Flow Quantities

Low Flow 2 gal/lb of hide Average Flow 6 gal/1b of hide High Flow 20 gal/1b of hide

Concentration Range Based on Average Flow

$$\frac{20 \times 10^{6} \text{ hides}}{\text{year}} \times \frac{50 \text{ lb}}{\text{hide}} = 1.0 \times 10^{9} / \text{yr}$$

$$\frac{1 \times 10^{9} \text{ lb}}{\text{year}} \times \frac{6 \text{ gal}}{\text{lb}} = \frac{6 \times 10^{9} \text{ gal}}{\text{year}} (\text{or } 50 \times 10^{9} \text{ lb H}_{2} \text{0/yr})$$

$$\frac{\text{Low Concentration}}{50 \times 10^9 \text{ lb } \text{H}_2^{0/\text{yr}}} = 22 \text{ ppm}$$

$$\frac{\text{High Concentration}}{50 \times 10^9 \text{ lb } \text{H}_2^{0/\text{yr}}} = 56 \text{ ppm}$$

Dye Concentration Based on Dyeing Operation Only (Float Average of 2/1)

$$\frac{\text{Low Concentration}}{\left(\frac{50 \text{ lb}}{\text{hide}}\right) \left(\frac{20 \text{ x } 10^6 \text{ hides}}{\text{yr}}\right) \left(\frac{2 \text{ lb } \text{H}_20}{\text{yr}}\right) = 560 \text{ ppm}}$$

$$\frac{\text{High Concentration}}{\left(\frac{50 \text{ lb}}{\text{hide}}\right) \left(\frac{20 \text{ x } 10^6 \text{ hides}}{\text{yr}}\right) \left(\frac{2 \text{ lb } \text{H}_20}{\text{yr}}\right) = 1400 \text{ ppm}}$$

Source: Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Leather Tanning and Finishing Point Source Category, EPA-440/1-74-016a, March 1974 and SRI International.



\*Based on 6 gal/lb of hide

SOURCE: Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Leather Tannery and Finishing Point Source Category, EPA-440/1-74-016a, March 1974.

tSince the dyes used in the leather industry are protein-binding and the waste streams have a high level of protein (hair, flesh, hide), it is probable that much of the dyes could be removed with the solids.

<sup>+</sup>This is an average of two values from souce in (a).

SOURCE: E. Weisberg, 1975. Development of a Waste Treatment System for a Tannery, AIChE Proc. of Workshop, Ind. Proc. Design on Pollution Control 7, 44-48 •

SA-5619-23

FIGURE 3 . EFFLUENT TREATMENT FOR A COMPLETE CHROME TANNERY



FIGURE 4 . ESTIMATES OF  $BOD_5$ , COD, AND TOC OF EFFLUENT STREAMS OF TANNERY

wastewater; however, if these organics are not removed in treatment, they could represent a significant portion of the soluble COD or TOC in the effluent.

From а review of the literature on biodegradability of dyes included in Appendix B to this report, it appears that biodegradation of the dyes is unlikely to be a mechanism for removal. Because of the high concentrations of other degradable organic compounds, however, it is possible to а large population of viable microorganisms. maintain Removal of dyes biosorption (perhaps with proteinaceous material) by by reaction cellular may be the major mechanism for removal of the dyes in the activated sludge A similar mechanism may be responsible unit. for any removal that occurs in the primary treatment unit where a portion of the suspended matter is composed of proteinaceous material (hair and hide scapes).

A large percentage of the dyes may be removed from the tannery in combination with waste primary and secondary sludge solids.

I

#### **SECTION 6**

#### TOXICITY AND ENVIRONMENTAL FATE OF DYES

## TOXICITY OF DYES

Because no data available on actual extent of removal of are the in treatment plants (industrial combined municipal/industrial) dyes or from tannery wastewaters, the next logical step in the analysis is to consider the toxicity of the dyes and the possible fate of the dyes the environment. in

### Toxicity to Acquatic Organisms

In study sponsored by the American Dye Manufacturers Institute, а Inc (ADMI 1974), more than 50 dyes were screened for toxicity to the Selenastrum capricornutum, and single-celled green algae, the fathead promelas). minnow (Pimephales This probably most comprehensive is the yet performed in the United States to the potential study assess hazdyes life. We considerable ards of to aquatic understand that a data base on the environmental effects of dyes has been developed in Japan; unable to obtain the data in time for however, we were this report,

The ADMI study showed that the basic dyes are generally more toxic Table 16 shows that of 15 basic dyes than the acid or direct dyes. tested, 13 inhibited the growth of 2. capricornutum by at least 80% at 1 mg/liter in 7 days. All 5 of the basic dyes screened with minnows had 96-hour LC50 concentrations of less than 6 mg/liter, as shown in Table 17. Basic Green 4 and Basic Violet 1 had 96-hour LC5Os of less 1 mg/liter. than

Some of the acid dyes exhibited relatively high toxicity to minnows. Most toxic of all 11 dyes tested were Acid Blue 113, Acid Green 25, Acid Black 7, and Acid Yellows 38 and 151. The 96-hour LC5Os for these dyes ranged from 4 to 29 mg/liter.

Of the three kinds of dyes, direct dyes were the least toxic to minnows. Of 14 direct dyes tested, none had a 96-hour LC50 less than 125 mg/liter, and most had LC5Os greater than 180 mg/liter. Direct Blacks 3% and 80 inhibited algal growth by at least 80% at 10 mg/liter.

		Concentration producing	Concentration producing
Dye		at least 50% inhibition	at least 80% inhibition
Acid Black	1	10	>10
Acid Blue	25	10	>10
Acid Blue	113	10	>10
Acid Green	25	10	10
Acia Green	25	10	10
Basic Blue	39	1	1
Basic Blue	9	1	1
Basic Blue	21	1	1
Basic Violet	1	1	1
Basic Violet	6	1	1
Basic Violet	10	10	>10
Basic Brown	4	10	10
Basic Orange	2	1	1
Basic Orange	21	1	1
Ba <b>sic</b> Red	2	1	1
Basic Red	18	1	1
Basic Yellow	11	1	1
Basic Yellow	13	1	1
Basic Yellow	37	1	1
Basic Green	4	1	1
Direct Blue	6	10	>10
Direct Blue	218	10	>10
Direct Brown	95	10	>10
Direct Black	38	10	10
Direct Black	80	10	10

TABLE 16. TOXICITY OF ACID, BASIC, AND DIRECT DYES TO THE GREEN ALGA, <u>SELENASTRUM</u> CAPRICORNUTUM

\* Based on biomass.

† In mg/liter.

Source: American Dye Manufacturers Institute, Inc. "Dyes and the Environment", Reports on Selected Dyes and Their Effects, Vol 2, Sept. 1974.

Dye		96-Hour LC50 (mg/liter)
Acid Orange	7	165
Acid Orange	24	130
Acid Yellow	17	>180
Acid Yellow	38	23
Acid Yellow	151	29
Acid Black	1	>180
Acid Black	52	7
Acid Blue	25	12
Acid Blue	45	>180
Acid Blue	113	4
Acid Green	25	6.2
Basic Brown	4	5.6
Basic Green	4	0.12
Basic Violet	1	0.047
Basic Yellow	11	3.2
Basic Blue	3	4.0
Direct Yellow	4	>180
Direct Yellow	11	>180
Direct Yellow	12	1 <b>2</b> 5
Direct Yellow	28	>180
Direct Yellow	50	>180
Direct Yellow	106	>180
Direct Blue	6	>180
Direct Blue	86	>180
Direct Blue	218	>180
Direct Red	23	>180
Direct Red	81	>180
Direct Brown	95	>180
Direct Black	38	>180
Direct Black	80	>180

TABLE 17. TOXICITY OF ACID, BASIC, AND DIRECT DYES TO THE FATHEAD MINNOW, <u>PIMEPHALES</u> PROMELAS

> Source: American Dye Manufacturers Institute, Inc., "Dyes and the Environment," Reports on Selected Dyes and Their Effects, Vol. 2, Sept. 1974.

The toxicity of dyes could berelated chemical to structure; howpreliminary inspection of the structures did not reveal obvious ever. any relationships. А more comprehensive evaluation is beyond the scope of this project.

Effluent from the leather industry contains, among other substances, a mixture of dves. We estimate that prior to treatment. the effluent contains about 22 to 56 mg/liter of total dyestuffs. It is difficult to determine how toxic this concentration range will be to aquatic organisms if it remains unchanged after treatment. The toxicity will depend on the kinds of dyes in the mixture and the interaction among the dyes and with other compounds in the effluent. We would expect the effluent aquatic organisms to be acutely toxic to if the mixture contained primarily basic dyes.

Before a meaningful hazard evaluation of the effluent can be made. information would have to be obtained regarding the interactive effects of the various dyes in the mixture. Furthermore, only acute toxicity data have been generated to date; chronic toxicity data are also needed.

found only a We limited amount of information on the bioaccumulation We potential of dyes. understand that this kind of information has been We high developed extensively in Japan. do not anticipate bioaccumulation potentials for the more polar dyes; however, since these dyes are used leather industry, and leather is composed primarily of proteins, in the some bioaccumulation is expected in aquatic animals.

Р partition The (octanol-water coefficient values) for log some azo indicating lipophilicity dyes are relatively high, high and therefore а bioaccumulate. azobenzene, 4-aminoazobenzene, 4-dimethyltendency to For 2-methyl-4-[(2-methylpheny1)azol benzenamide, aminoazobenzene. and the log P values 3.50, 4.58, and 4.24, respectively. are 3.82, Other nonhigh bioaccumulation potential polar dyes may have а also.

### Potential Human Health Effects

Few toxicological studies laboratory mammals with have been performed on dyes specific the leather industry; hence. to no positive conclusions can be made concerning the impact of these dyes on human However, many of the dyes are aromatic health. amines, a class of comnumber carcinogens. pounds comprising а large of suspected Other dyes which, cleaved, possess diazo groups, if could be converted to aromatic amines. Still others contain aromatic nitro groups that are characteristic of compounds with carcinogenic potential.

Dyes that have been shown to be carcinogenic in rodents include Basic Orange 2 and Direct Blue 14 (IARC, 1975). Information reported may be carcinogenic in the IARC Monograph indicates that Direct Blue 53 teratogenic. Studies have been performed on Acid Red 2 and Acid and Orange 20, but the data are inadequate for judging the potential of to produce cancer. these dyes

### ENVIRONMENTAL FATE

There are few data on which to base an environmental fate assessfor dyes introduced into waters by the leather industry. This is ment due in part to the large number of dyes used, which may be complexed by any of several metal ion species either in the dyeing plant or later in aquatic environment. The mixtures of dyes<sub>\*</sub> also contain the impurities. which adds the complexity of the assessment. Additionally, the into dustry itself has had no facilities for determining the composition of the effluent Most of the dyes used in the leather streams. industry are protein-binding dyes and the waste streams in a tannery containing other materials hair, flesh, trimmings, and are high in protein and could be expected to bind many of the dyes and thus remove them from stream. This process, however, would probably depend on the pH and the chemical composition of the effluent stream.

### Physical Properties

available, in No physical properties were part probably because the impurities in dyes themselves make measurements of data question-From the general structure of various dyes, of which able. some contain phenolic, amine, sulfonic acid, and other ionic groups, these dyes should be moderately soluble in water; no quantitative information was found.

## Chemical Transformation

#### Hydrolysis

Dyes contain no common group that is subject to hydrolytic reactions. Some dyes do contain acetylated amine groups on aromatic rings, and such can be hydrolyzed at pH 7 at  $\sim 20^{\circ}$ C with half-lives of a year or more

<sup>\*</sup> Ecological Toxicological Association of Dyestuff Manufacturand the Industry (ETAD), based in Switzerland, apparently has ing data on the environmental fate of dyes which may provide information. some This information is being sought.

and Mill, 1978). Since such reactions slow. only affect (Mabey are and minor part of the dye structure, hydrolysis should not be considered a important an fate.

### Oxidation

No information on the environmental oxidation of any dye was available.

### Photolysis

Porter (1973) has conducted photolyses of dyes in neutral water solutions. Most photolyses were performed using a carbon-arc light which partially simulates the wavelengths source. and distribution of followed the solar spectrum. The photolyses were by decreases in absorbance at wavelengths in the visible region. The data were plotted (concentration) bv Porter as versus (time): straight-line plotted in а this manner indicates a zero-order kinetic law behavior. Most of the plots were not linear, however, and showed curved lines, a few of which may be first order if replotted as ln (concentration) versus (time). also with the dyes Basic Green 4 and Direct Photolyses were conducted photolysis Blue 76 sunlight. data for and carbonin The the sunlight arc light experiements are summarized in Table 18.

half-life data obtained from this data Meaningful cannot be since coherent kinetic law behavior was found; this could have been due to no number of reasons, including the impurity of the dyes themselves with a the compounds present reacting at different rates and possibly also with each other and/or products. The analytical method must also be respongood sible for the failure to get kinetic plots some dyes for since at a wavelength measured, which included only the total absorbance was absorbances of the dye, impurities, and products. Moreover, since the leather dye process often uses metal ions other those used in the than photochemical due diftextile processes, some rates may be different to ferent metal ions present: Porter's work used the textile dves. Porter states that the carbon arc light gives photolysis rates that are at least 10 times faster than those in sunlight. Using this rough rule of thumb, and assuming that the photolysis rate varies linearly with light the amount of reaction indicated in Table 18 with the carintensity. about 6 months of sunlight (at 12 hours of bon arc lamp corresponds to sunlight per day). As seen in Table 18, most dyes will be resistant photodegradation with half-lives of least а few months at or more. to appears that the basic most photodegradable, acid It dyes are the dyes are of varying reactivity, and the direct dyes are the least photoreactive.

		% Reaction
		after
		200 hr
		with
		carbon .
Basic Dyes		arc lamp <sup>*</sup>
	•	70
Basic Violet	3	/8
Basic Blue	9	58
Basic Green	1	90 <sup>+</sup>
Basic Green	4	92
Basic Red	2	71
Acid Dyes		
Acid Red	1	30
Acid Violet	3	92
Acid Orange	10	>95
Acid Red	37	>95
Acid Black	52	< 8
Acid Violet	43	50
Acid Blue	40	<10
Direct Dyes		
Direct Red	80	0
Direct Green	6	27
Direct Black	80	30
Direct Blue	76	87‡
Direct Blue	98	30
Direct Red	83	50
Direct Brown	95	40
Direct Blue	86	10
* Using rule o	f thumb	o that carbon arc lamp gi

\* Using rule of thumb that carbon arc lamp gives photolysis rates 10 times that of sunlight(see text), the % reaction also corresponds to exposure to 2000 hr sunlight, or 6 months at 12 hr of sunlight per day.

t

# † In sunlight, 44% of Basic Green 4 was consumed after 1600 hr of exposure.

‡ In sunlight, 50% of Direct Blue 76 was consumed after 1600 hr of exposure.

#### Physical Transport

### Volatilization

Volatilization should not be an important fate for dyes since they should be quite soluble in water and have low vapor pressures.

#### Sorption by Particulate Matter and Biota

Since dyes seem to have long half-lives in relation to other environmental processes, sorption may be an important fate in spite of the expected moderate water solubility of the general class of dyes.

#### Biodegradation in the Environment

The amine and phenolic groups in many of the dyes suggest a potential for facile aerobic biodegradation. However, our discussions with Dr. Samuel Boyd of Du Pont and Dr. J. J. Porter of Clemson University have led us to conclude that biodegradation is not rapid. One factor influencing the biodegradation may be metal ions that complex the various functional groups. In any event biodegradation rates are difficult to predict for *any* chemical in the aquatic environment since the season and characteristics of the discharge-receiving water will vary considerably and affect its biodegrading capability.

The probable fate for dyes introduced into aquatic environments is to remain in solution in the water system, with sorption onto sediments and biota eventually occurring. Chemical processes or volatilization of dyes do not appear to be important fate processes for most dyes. Long-term biodegradation in sediment probably does eventually transform most dyes, but the absence of relevant data prevents quantitative evaluation of such processes.

#### REFERENCES

American Dye Manufacturers Institute, Inc., 1974. Dyes and the Environment, Reports on Selected Dyes and Their Effects, Vol. 2.

Caldwell Lace Leather Co., 1977. Private Communications.

- Environmental Protection Agency, 1974. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Leather Tanning and Finishing Point Source Category, EPA-440/1-74-016a.
- Etzel, J. E., and C.P.L. Grady, Jr., 1973. Effects of Dyes on the Anaerobic Digestion of Primary Sewage Sludge. In: Dyes and the Environment-Report on Selected Dyes and Their Effects, report for the American Dye Manufacturers Institute, Vol. 1, Chap. VII.
- Fung, D.Y.C., and R.D. Miller, 1973. Effects of Dyes on Bacterial Growth, Appl. Microbiol. 25:793-799.
- Hunter, J.V., 1973. The Effect of Dyes on Aerobic Systems. In: Dyes and the Environment-Report on Selected Dyes and Their Effects, report for the American Dye Manufacturers Institute, Vol. 1, Chap. VI.
- International Agency for Research on Cancer, 1975. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man, Vol. 8, Lyon.
- Mabey, W., and.T. Mill, in press. J. Phys. Chem. Ref. Data
- Porter, J. J., 1973. A Study of the Photodegradation of Commercial Dyes, PB-221483.
- Porter, J. J., and E. H. Snider, 1976. Long-Term Biodegradability of Textile Chemicals, J.W.P.C.F. 48:2198-2210.
- Porter, J. J., and E. H. Snider, 1975. Thirty-Day Biodegradability of Textile Chemicals and Dyes. In: Amer. Assoc. of Textile Chemists and Colorists, Tech. Papers of the Nat'l. Tech. Conf., October 15, pp. 427-36.

Thackston, E. L., 1973. Secondary Waste Treatment for a Small Diversified Tannery. EPA-R2-73-209.

## APPENDIX A

## DYES USED IN THE LEATHER INDUSTRY

Inventory lists from two tanneries showed a variety of dyes in stock, including several not usually listed by suppliers as being used in the leather industry. The major suppliers are Ciba-Geigy, Sandoz, Crompton & Knowles, Verona, GAF, BASF, American Cyanamid, and American Color. Dyes used are acid, basic, direct, and some solvent dyes. Metallized dyes are also used to obtain a specific product. Some of the dyes used are given in Table 19.









. Name	CAS No.	Structural Formula	Empirical Formula	C.I. No.	Remarks	1 1
e	118-26-3; 1934-21-0; 34175-08-1	$NaO_3S - $ $NaO_3S - $ $NaO_3S - $ $NaO_3Na$ $NaO_3S - $ $NaO_3Na$	<sup>c</sup> 16 <sup>H</sup> 9 <sup>N</sup> 4 <sup>Na</sup> 3 <sup>0</sup> 9 <sup>S</sup> 2	19140		
77	605-69-6; 887-79-6; 10142-54-8	COON a COON a $(NH_4, Na, or Ca/2)$	C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>5</sub> (or C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O <sub>5</sub> 'NH <sub>4</sub> , Na, or Ca/2)	10315		
36	4005-68-9; 587-98-4		C <sub>18</sub> <sup>H</sup> 14 <sup>N</sup> 3NaO <sub>3</sub> S	13065		
64	6372-96-9	$H_{3}^{C} - \left( \sum_{i=1}^{N} -SO_{2} \cdot 0 - \left( \sum_{i=1}^{N} - \left( \sum_{i=1}^{N}$	c <sub>22</sub> H <sub>18</sub> cin4Na0 <sub>7</sub> s <sub>2</sub>	18950		
7	24382-22-7	$\bigcup_{N=0}^{N-C} N = N - \bigcup_{N=0}^{C-N} N = N $				
сл сл	10343-58-5	$\begin{array}{c} \begin{array}{c} CH_{3} \\ $	C <sub>32</sub> H <sub>2</sub> 4 <sup>N</sup> 8 <sup>Na</sup> 2 <sup>085</sup> 2 C <sub>16</sub> H <sub>13</sub> N <sub>4</sub> Na085	22910 13900	Cr <sup>+++</sup> complex used	

Remarks		Zinc double chloride complex				
C.I. No.	13906	51175	52015	21010	21010	42000
Empirical Formula	c <sub>16</sub> H <sub>16</sub> N4o5s	c <sub>18</sub> <sup>H</sup> 13 <sup>C1N</sup> 2 <sup>0</sup>	c <sub>16</sub> H <sub>18</sub> CIN <sub>3</sub> S	C18 <sup>H</sup> 18 <sup>N</sup> 8	c <sub>15</sub> H <sub>24</sub> N <sub>8</sub>	c <sub>23</sub> H <sub>19</sub> cin <sub>2</sub>
Structural Formula	$H_2^{N} \cdot O_2^{S}$	$(H_3C_2 N \sqrt{C_1 N} = 0$	$(H_3C)_2 N - \underbrace{\left( \bigcap_{S=1}^{N} \prod_{S=1}^{n} \bigcap_{S=1}^{n} N(CH_3)_2 \right)}_{-C1}$	$H_2^{N} - \underbrace{\bigvee_{i=1}^{NH_2}}_{i=1} = \underbrace{N - \underbrace{\bigvee_{i=1}^{NH_2}}_{i=1} = N - \underbrace{N $	$H_2N - 6N + 2N +$	$c_{6}H_{5}c$ $c_{1}S_{5}c$ $c_{1}S_{5}c$ $c_{1}S_{5}c$ $c_{1}S_{5}c$ $c_{1}S_{5}c$ $c_{1}S_{5}c$
CAS No.	12715-61-6	7057-57-0	61-73-4	1052-38-6	4482-25-1	56 <b>9-</b> 64-2
C. I. Name	Acid Yellow 151	Basic Blue 6	Basic Blue 9 (Methylene blue)	Basic Brown 1	Basic Brown 4	Basic Green 4 (Malachite Green)

59

.

Remarks					
<u>с.1. No.</u> 11320	11270	42535	42555	45170	45175
Empirical Formula C <sub>13</sub> H <sub>1</sub> SCIN4	c <sub>12</sub> H <sub>13</sub> cIN4		с <sub>25</sub> <sup>н</sup> 30 <sup>сци</sup> 3	C <sub>28</sub> <sup>H</sup> 31 <sup>CLN</sup> 2 <sup>O</sup> 3	с <sub>30</sub> <sup>н</sup> 35 <sup>с</sup> 1и <sub>2</sub> <sup>0</sup> 3
Structural Formula $ \sum_{N=N}^{NH} = N - \sum_{CH=0}^{N+1} + \frac{1}{N} \int_{CH=0}^{1} CH^{2} $	$\sum_{n=N-N-N-1}^{NH_2} \sum_{n=N-1}^{3} \sum_{n=1}^{3} \sum_{n=$		$(H_3C)_2 \xrightarrow{N-C} (H_3C)_2 \xrightarrow{+} (CH_3)_2 \xrightarrow{+} (CH_3)_2 C\overline{1}$	$(H_5^{c_2})_2^{N} \bigwedge_{f = 0}^{t_2} \left[ \begin{array}{c} 0 \\ c \\ f \\ f$	$(H_5c_2)_2 N (M_5c_2)_2 N (M_5c_2)_2 = N(c_2H_5)_2 C_{11}$
CAS No. 5042-54-6 4438-16-8	495-54-5; 532-82-1	8004-87-3	548-62-9	81-88-9	2390-63-8
C.I. Name Basic Orange 1	Basic Orange 2 (Chrysoidine)	Basic Violet l (Methyl violet)	Basic Violet 3 (Crystal violet)	Basic Violet 10	Basic Violet 11

60



61

### Appendix B

## BIODEGRADATION OF DYES IN BIOLOGICAL TREATMENT SYSTEMS

Very little information on biodegradation is available; hence, this appendix is primarily a discussion of the potential for dyes to biodegrade in biological treatment systems.

Most of the dyes used in the leather industry contain sulfonic acid, sulfonamide, phenolic, and and/or nitro functions. Their colors are azo attributed to the characteristics of the conjugated unsaturated strucand the dyeing characteristics are attributed to the binding tures. capacities of these compounds to the protein in the leather, particularly the acid functions. Proprietary mixtures frequently with sulfonic are used to obtain the desired colors. The preparation of these dyes frequently requires the use of chemicals that are considered toxic and some of the dyes must themselves be regarded as potential toxic substances. All living cells contain proteins in their wall membranes, and if staintakes place, it indicates combination of the pigmented product with ing the protein. This may interfere with the physiological processes of the Fortunately, not all products used in coloring are toxic and some cell. actually essential for physiological functions: such products include are riboflavin, vitamin A and the carotenoids, the cytochromes, the heme pigments, chlorophyll, vitamin B 12 analogues, and many other compounds. Other dyes are useful indicators of oxidation-reduction or pH and are not di-sodium-phenol-tetrabromophthalein in themselves toxic. Sulfonates such as in protein analysis because, disulfonate (Bromsulfalein) have been used conditions, they readily precipitate proteins. under acid

There are biological counterparts to the above chemicals that contain enzymes that can reduce such chromophoric structures as azo, quinone, and nitro compounds; however, these enzymatic reactions are highly specific the structures of susceptible substrates. If novel substrates are exto biodegradability or persistence, aerobic amined for by or anaerobic procperiods of acclimation of a large microbial population are required, esses, are complex processes that are not adequately understood, but with These co-metabolism or diauvic growth phenomena some relatively simple compounds have been observed. Even under seemingly oxidative conditions, reductive processes such as the transformations of R-NO<sub>2</sub> to R-NH<sub>4</sub> or R'Cl to R'H can take place. These reductions occur because of the availability of reduced coenzymes from other oxidative processes. If the dyes used
industry are decomposed, functions in the leather tanning the nitro and azo yield finally amino compounds. compounds are are reduced to These amino then deaminated to form ammonium ions and the nitrogen is finally oxidized Aromatic nuclei oxidized catechols ring to nitrate. are to and the structures are subsequently ruptured to vield products that are generally more readily metabolized.

possible residual in the wastewaters It is also that dyes from dveing processes may stain or combine to some extent with the organisms in an actrickle filter sludge plant, plant, or anaerobic digestors, at contivated centrations do seriously affect waste treatment organisms, and by that not this means dves can be removed from the plant effluents.

Miller (1973) studied the effects of 42 dyes on the growth Fung and that of 30 bacteria in solid media. and it is apparent the gram-negative bacteria they used were more resistant that the gram-positive bacteria. Biodegradation studies conducted in other laboratories and in SRI laboraresulted development of enrichment cultures that contories have in the gram-negative bacteria, but gram-positive bacteria fungi tain mostly and also been found to be excellent degraders or transformers of some have compounds. One of the problems the tanneries have to cope with is the use of some dyes, and if extensive acclimation periods sporadic are necdevelop biodegrading flora to degrade the dyes. the degrading essary to are lost by microbial interaction and а fresh charge а dve organisms of decomposed. If the dye concentration is be initially too high to mav not facilitate the development of the necessary flora, the dye might even desreadily If troy some of the existing organisms. too much metabolizable oils) material (e.g., proteins, particles. fats and is present in the inplant fluent to the treatment after the customary pretreatments, the resiin dence time of the dve the treatment plant may not be sufficiently long diauxic phenomenon exists, or the dye may be recalcitrant by customif а ary parameters.

The shortcomings of 5-day BOD test are clearly discussed in the publications by Porter and Snider (1975, 1976). However, other factors may involved proteins be because of the presence of fats, oils, surfactants, that are present in larger and peptides amounts and are more rapidly metabolized than the dyes.

V. Hunter (1973)studied the effect of dyes on aerobic waste J. treatment systems and concluded that 17 out of 46 dyes inhibited action of acconducted Warburg tivated sludge in aerobic processes in flasks with activated sludge, water organic matter, and the dyes. This report river not imply that the had but it indicated some did processes ceased, that activity continued а reduced rate. Small samples and relatively high at mg/liter) levels of dyes (25 were used in this work. With some dyes,

inhibition digestion observed with sewage-dye-activatedof was only the same publication. Etzel and Grady (1973) reported sludge. In that two anthraquinone dves had strong enough activity to cause failures in laborascale anaerobic digesters. The concentration of dve added was 150 mg/ tory agent Tamo-SN also similar acute effect. liter The dispersing had а . Other dyes showed some effects. but these were not sufficiently serious cause disruption of the anaerobic Decolorization was obto processes. served with all but two dyes.

In an EPA report on leather tanning and finishing and numerous other publications, reference is made to the use of activated carbon to remove residual the problems of the application of such adsorption dyes and processes tannery-plant other to effluents containing products that interremoval. If tannerv effluents with dve are highly diluted fere with color is possible with municipal wastewaters, it that they are eliminated by activated sludge and may escape attention because this adsorption on of high dilution.

reviewed The current literature in this brief survey indefinite is too to form a basis for a conclusion on the best procedures to handle dyes present tannery wastes. Longer biological treatment periods, or rein cycling trickling filter units for specific dyes improve of the may some current biological treatment facilities. It may also be necessary to effluents extensively change chemicals treat more or to some processes or economically before activated carbon can be and efficiently used. A more extensive literature and field analysis is necessary and experimental undoubtedly required. verification of control technology will be

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)					
1. REPORT NO. 2.		3. RECIPIENT'S ACC	ESSION NO.		
EPA-600/2-78-215					
4. TITLE AND SUBTITLE		5. REPORT DATE			
Assessment of Potential Toxic Releases	From Leather	Uctober 19/8 issuing date			
Industry Dyeing Operations		6. PERFORMING OR	GANIZATION CODE		
		8 PERFORMING OR	GANIZATION REPORT NO.		
S.B. Badding J.F. Jones W.P. Mohow D	U T	0,1 2,11 0,111 0 0.11			
N Bobonos	• E• Li±u,				
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEN	IENT NO.		
SRI International		188610			
333 Ravenswood Avenue		11. CONTRACT/GRANT NO.			
Menlo Park, CA 94025		R 804642-01-2			
nonico non grocy		N 004042-01	-2		
12. SPONSORING AGENCY NAME AND ADDRESS		13. TYPE OF REPOR	T AND PERIOD COVERED		
Industrial Environmental Research Lab Cinn OH		Final Report 6/77 - 4/78			
Office of Research and Development	oinn, on	14. SPONSORING AGENCY CODE			
U.S. Environmental Protection Agency		EPA/600/	12		
Cincinnati, Ohio 45268		2111, 000,			
15. SUPPLEMENTARY NOTES					
16. ABSTRACT					
This study focused on the organic	dyes released	d to the envi	ronment in		
the wastewaters from leather dyeing open	rations. Bas:	ically, three	types of		
dyesacid, basic, and directare used	, although the	e number of d:	ifferent		
dyes are well over 50, and the number of	f formulations	s used at a si	ingle		
tannery over the period of several years	s can be great	ter than 100.	Tannerv		
wastewaters are complex mixtures which	for the most i	oort ore dicol	hongod		
dinostly into municipal covers. The she		valt ale uist			
diffectly into multipar sewers. The cha	aracter of th.	is discharge v	NIII		
allier nourly depending on the operation	n performed s:	ince tanning (	operations		
are batch mode. Estimates based on info	ormation from	suppliers and	l tanners		
were made of the probable discharge of d	lyes in wastew	water. The li	iterature		
search revealed little or no data on the	e fate of the	se dyes in the	e environ-		
ment. From consideration of the physica	al and chemics	al properties	of the		
dyes, biosorption (complexing with prote	dves, bioscription (complexing with proteinaceous material) appears to be				
the most likely mechanism for removal of dyes in biological wastewater					
treatment systems.					
This report covers the period 1 June 1977 to 28 April 1978 and was					
completed as of 28 April 1978.					
17. KEY WORDS AND DO	CUMENT ANALYSIS		- COOATLEistd/Crown		
a. DESCRIPTORS	b.IDENTIFIERS/OPI	EN ENDED TERMS	c. COSATI Field/Group		
Industrial Wastes, Wastewater,	Lesther Ta	nning	13B		
Toxicity, Organic Compounds,	neather it				
Dyeing					
18 DISTRIBUTION STATEMENT	19. SECURITY CLA	SS (This Report)	21. NO. OF PAGES		
	Unclassifi	ed	73		
Release to Public	20. SECURITY CLA	SS (This page)	22. PRICE		
	Incloseifi	64			
		. çu			

TECHNICAL R (Please read Instructions on th	EPORT DATA ae reverse before completing)			
1. REPORT NO. 2.	3. RECIPIENT	S ACCESSION NO		
EPA-600/2-78-215		O.		
4. TITLE AND SUBTITLE	5. REPORT DA	5. REPORT DATE		
Assessment of Potential Toxic Releases	From Leather Octobe	October 1978 issuing date		
Industry Dyeing Operations	6. PERFORMIN	NG ORGANIZATION CODE		
	8. PERFORMIN	NG ORGANIZATION REPORT NO		
S.B. Radding, J.L. Jones, W.R. Mabey, D N. Bohonos	. H. Liu,			
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM	ELEMENT NO.		
SRI International	1BB610			
333 Ravenswood Avenue	11. CONTRAC	T/GRANT NO.		
Menlo Park, CA 94025	R 804642	R 804642-01-2		
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF F	REPORT AND PERIOD COVERED		
Industrial Environmental Research Lab	Cinn, OH	Final Report 6/77 - 4/78		
Office of Research and Development	14. SPONSORI	NG AGENCY CODE		
U.S. Environmental Protection Agency	EPA/	600/12		
Cincinnati, Ohio 45268				
15. SUPPLEMENTARY NOTES				
16. ABSTRACT				
This study locused on the organic dyes released to the environment in the wastewaters from leather dyeing operations. Basically, three types of dyesacid, basic, and directare used, although the number of different dyes are well over 50, and the number of formulations used at a single tannery over the period of several years can be greater than 100. Tannery wastewaters are complex mixtures which for the most part are discharged directly into municipal severs. The character of this discharge will differ hourly depending on the operation performed since tanning operations are batch mode. Estimates based on information from suppliers and tanners were made of the probable discharge of dyes in wastewater. The literature search revealed little or no data on the fate of these dyes in the environ- ment. From consideration of the physical and chemical properties of the dyes, biosorption (complexing with proteinaceous material) appears to be the most likely mechanism for removal of dyes in biological wastewater treatment systems. This report covers the period 1 June 1977 to 28 April 1978 and was completed as of 28 April 1978.				
17. KEY WORDS AND DO	CUMENT ANALYSIS			
a. DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TEI	RMS C. COSATI Field/Group		
Industrial Wastes, Wastewater, Toxicity, Organic Compounds, Dyeing	Leather Tanning	13B		
		21 NO DE PACES		
18. DISTRIBUTION STATEMENT	Unclassified	73		
KELEESE TO PUDIIC	Unclassified			

.

U.S. ENVIRONMENTAL PROTECTION AGENCY Office of Research and Development Environmental Research Information Center Cincinnati, Ohio 45268

OFFICIAL BUSINESS PENALTY FOR PRIVATE USE, S300 AN EQUAL OPPORTUNITY EMPLOYER

> POSTAGE AND FEES PAID U.S. ENVIRONMENTAL PROTECTION AGENCY EPA-335



Special Fourth-Class Rate Book



If your address is incorrect, please change on the above label tear off; and return to the above address. If you do not desire to continue receiving these technical reports, CHECK HERE ; tear off label, and return it to the above address,

EPA-600/2-78-215