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Assessment of Potential Toxic Releases from Leather Industry Dyeing Operations

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October 1978

ASSESSMENT OF POTENTIAL TOXIC RELEASES FROM LEATHER INDUSTRY DYEING OPERATIONS

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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.

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ABSTRACT

This study focused on the organic dyes released to the environment in the wastewaters from leather dyeing operations. Basically, three types of dyes--acid, basic, and direct--are 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 sewers. 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 environment. 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.

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SECTION 1

INTRODUCTION

This report describes a study undertaken 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 the problems associated with the high BOD suspended material, and chrome chemicals in the effluent. This work focuses only on organic dyes.

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

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 ($\sim 7 \times 10^6$ lbs/year or 3.2×10^6 kg/year) and the average uptake for dyes (60-85%), it was estimated that total leather dye releases may range from $1.1\text{-}2.8 \times 10^6$ lbs/year or $0.5\text{-}1.3 \times 10^6$ 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/ℓ) 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

SIZE AND STRUCTURE

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

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

Environmental Impacts

Processing Operations

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

Beamhouse Process

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

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

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

No. of establishments									
		All employees		Production workers					
Total	With 20 employees or more	Number (10^3)	Payroll ($\$10^6$)	Number (10^3)	Man-hours (10^6)	Wages ($\$10^6$)	Value added by manufacture ($\$10^6$)	Cost of materials, fuels, etc. ($\$10^6$)	Value of industry shipments ($\$10^6$)
517	223	25.7	200.0	22.1	41.9	$151.3	$368.3	$708.0	$1,059.5

Source: U.S. Department of Commerce, Census of Manufacturers, 1972.

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

States	No. of 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	1	64,000
Washington	2	
Colorado	2	
Utah	1	1,015,638
Minnesota	2	
Nebraska	1	
Missouri	2	
Louisiana	1	33,152
Florida	2	
Virginia	1	
Delaware	1	437,386
Ohio	1	
Vermont	1	
Maryland	1	
TOTAL		17,491,282

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

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

States	No. of Plants	Production
Kentucky	3	490,750
Pennsylvania	4	925,043
Indiana	2	101,841
Ohio	1	
Virginia	1	1,000,271
West Virginia	1	
North Carolina	2	
Georgia	1	535,371
Tennessee	2	
Texas	1	
Oregon	1	
TOTAL		3,053,276

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

TABLE 4. 1976 PRODUCTION RATES IN EQUIVALENT SHEEP HIDES*

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

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

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

States	No. of plants	Production
Massachusetts	13	1,218,183
Wisconsin	5	1,394,605
California	1	
Illinois	1	957,827
New Hamshire	1	
TOTAL		3,570,615

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

TABLE 6. 1976 PRODUCTION RATES IN EQUIVALENT BLUE HIDES*†

States	No. of plants	Production
Colorado	1	
Arizona	1	
Iowa	2	2,181,000
Minnesota	1	
Missouri	1	
New Jersey	1	
Massachusetts	1	
TOTAL		2,181,000

* One equivalent hide ≃ 40 ft^2 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.

TABLE 7. 1976 PRODUCTION RATES IN EQUIVALENT RETAN/FINISHER HIDES*†

States	No. of plants	Production
Pennsylvania	3	95,000
Massachusetts	6	720,000
New York	3	255,000
New Jersey	3	80,000
California	2	731,254
Tennessee	1	
Wisconsin	1	
TOTAL		1,881,254

* One equivalent hide $\simeq 40\ ft^2$ 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.

TABLE 8. 1976 PRODUCTION EQUIVALENT FINISHED HIDES* †

States	No. of plants	Production
Massachusetts	22	2,550,000
New York	12	1,075,000
New Jersey	10	482,356
Ohio	3	57,981
California	1	
Tennessee	1	
Delaware	2	615,000
North Carolina	1	
New Hampshire	1	
Wisconsin	1	
TOTAL		4,780,337

* One equivalent hide $\simeq$ 40 ft^2 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.

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

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

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

(4) Washing and Soaking - Sides (or in some cases whole hides) from the siding and trimming operation are placed in vats (with or without paddles), drums, or hide processors (concrete mixers with special linings) for washing and soaking to restore moisture. Water usage is generally less with hide processors, although some tannery people have expressed the opinion that equivalent reduction in water use can be achieved with drums. This process removes dirt, salt, blood, manure, and nonfibrous proteins from the hides. The quantity of such waste material varies, depending on the time of year and the source of the hides. Depending on the type of leather produced, additional washes (rinses) may also occur at several other points in the tanning process, including after liming and dehairing, after bating, after tanning, and prior to and following coloring.

(5) Fleshing - Fleshing is the removal of attached adipose fatty tissue and meat that have been left on the hide at the packing house. It is done on a fleshing machine, in which the hide is carried through rolls and across rotating spiral blades that remove the flesh from the hide. Cold water is necessary to keep the fat congealed, but the fat represents an additional waste disposal load. Most hides are fleshed at the packing house or at a separate hide processing facility, particularly in the case of brined hides. When flesh is removed prior to liming it is referred to as green fleshing; when it is performed after liming it is referred to as lime fleshing. In any case, fleshings are normally recovered and sold to plants for rendering or conversion to glue. If fleshings are properly handled, there is very little liquid or solid waste contribution from this operation.

(6) Unhairing - Hair is removed by chemical loosening followed by either machine pulling or chemical dissolution of the hair. Machine removal is practiced when the processor desires to recover the hair. The dissolving process is referred to as "pulping" or "burning."

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

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

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

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

Tanhouse Process

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

a. De-lime skins.

b. Reduce swelling.

c. Peptize fibers.

d. Remove protein degradation products.

(2) Pickling - The pickling subprocess follows the bating step and is normally done in the same equipment. A brine and an acid solution is used to bring the hides to an acid condition in preparation for subsequent tanning subprocesses. In addition to conditioning the hide for receiving the tanning agent, this step prevents precipitation of chromium salts. Pickling is always done before the chrome tanning process and may be done before vegetable tanning.

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

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

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

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

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

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

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

Retan, Color, Fatliquor Process

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

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

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

(4) Fatliquoring 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.

TABLE 9. SUPPLIERS OF CHEMICALS TO THE TANNING INDUSTRY

Allied Chemical Corp.	Staley Chemical Division
American Cyanamid Co.	Tac Tannins & Chemicals, Inc.
Atlas Refinery, Inc.	Arthur C. Trask Corp.
Barkey International Corp.	Union Carbide Corp.
BASF Wyandotte Corp., Carlstadt Leather Fin.	Verona Dyestuff Div., Mobay Chem. Corp.
Birko Chemical Corp.	Wayne Chemical Corp.
Chemical Coating Materials Co.	Weber & Smith, Inc.
Ciba-Geigy Corporation	Whittemore-Wright Co., Inc.
Eastern Industrial Oil Prod. Co., Div. of Henkel, Inc.	Eric C. Baum Assoc., Inc.
Industrial Chemical Co.	Hamblet & Hayes Co.
Kepec Chemical Co.	The Hine Line
Kepec Div. of Hendel, Inc.	Hooker Chemicals & Plastics Corp.
L. H. Lincoln & Son, Inc.	Industrial Commodity Corporation
Marden-Wild Corporation	International Advisory Service
Diamond Shamrock, Napco Chemical Div.	Johnson & Carlson
A. J. & J. O. Pilar, Inc.	Korium Associates, Inc.
Pilar River Plate Corp.	Norton Co.
PPG Industries, Inc.	Quaker City Hide Co.
Prime Leather Finishers Co.	Redi-Stac, Inc.
K. J. Quinn & Co., Inc.	The Roit Corporation
Rohm & Haas Company	Chas. H. Stehling Co.
Salem Oil & Grease Co.	Arthur C. Trask Corp.
Sandoz Colors & Chemicals	USM Corp-Turner Tanning Machinery Div.
Samuel Smidt Chemical Corp.	Woburn Machine Co.
Stahl Finish - Beatrice Chem. Div. of Beatrice Foods 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.

TABLE 10. SUPPLIERS OF HIDES AND SKINS

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 Brokerage Corp.
Cahen Trading Co., Inc.	B. N. Ritter & Co.
George P. Cavanaugh, Inc.	Rockford Hide Co.
Chilewich Corp.	St. Louis Hide Co.
Herbert A. Cohen Co.,	Frank J. Schwab Associates, Inc.
Denison Hide Co., Inc.	Sklut Hide & Fur Co.
Dietrich Hide Corporation	Southern Tier Hide & Tallow, Inc.
Eden & Strass, Inc.	Southwestern Trading Company
H. Elkan & Company, Mass.	Spencer Foods, Inc.
H. Elkan & Co., Ill.	Swift Fresh Meats Co. - Hide Division
George H. Elliott Company	Transcontinental Industrial Co., Inc.
Estra Trading Company	Union Hide Company, Inc.
Evansville Technical Corp.	A. L. Webster Co.
Paul Gallagher & Co., Inc.	WeCo
Fred Gruen Co., Inc.	Western Hide Co., Inc.
Hickman & Clark, Inc.	G. A. Wintzer & Son Co.
Hide Service, Inc.	
J. C. Hodges & Co., Inc.	
A. J. Hollander & Co., Inc.	
Kaufmann Trading Corp.	

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 process not only reduces pollution but also produces quality leather at a lower cost. Cyanides have also been eliminated according to industry 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 tanning, the potential exists for both water and solid wastes. Materials that can appear in tannery wastes are listed below:

Hair	Salts
Hide scraps	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 10^6 lb dye/yr (1.36 to 3.18 x 10^6 kg/yr); the calculation based on data from tanning industry representatives indicates use could be as high as 30 x 10^6 lb dye/yr (13.6 x 10^6 kg). However, it is felt that an estimate of 7 x 10^6 lb (3.18 x 10^6 kg) annually is more realistic based on the number of hides dyed and the average dye loading to the dyeing operation.

Pollutant Sources

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

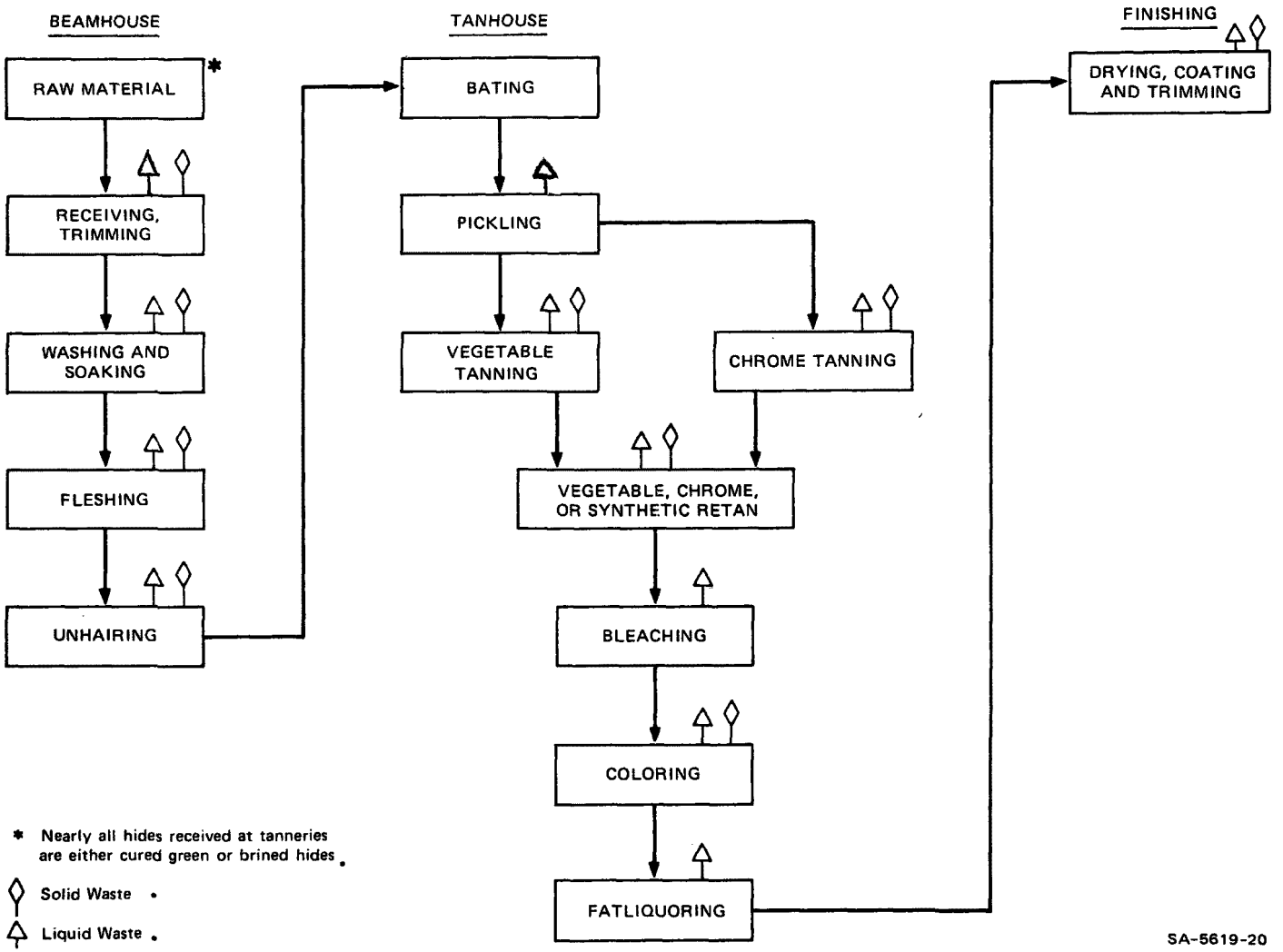


FIGURE 1. FLOW DIAGRAM FOR LEATHER TANNING PROCESS.

TABLE 11. CHEMICALS USED IN LEATHER PROCESSING

- Beamhouse Process
  - Soaking
    - Disinfectants
    - Nonionic surfactants → Alkanol ethoxylate; Alkylphenyl ethoxylate
    - Soda ash (sodium carbonate)
    - Sodium polysulfide (tetra)
    - Sodium sulfide
  - Liming (Unhairing)
    - Calcium chloride
    - Sharpening agents → Sodium sulfides → Sodium hydrosulfide; Sodium sulfite; Amines → Dimethylamine sulfate; Cyanides
    - Lime
    - Proteolytic enzymes
    - Nonionic surfactants → Alkanol ethoxylate; Alkylphenyl ethoxylate
  - Bating
    - Ammonium sulfate
    - Ammonium chloride
    - Formic acid and salts → Sodium formate
    - Proteolytic enzymes → Oropon bates (Rohm & Haas Co.)
    - Nonionic surfactants → Alkanol ethoxylate; Alkylphenyl ethoxylate
  - Degreasing
    - Sheepskin and pigskin degreased after bating → Kerosene; Stoddard solvent; Nonionic surfactant → Alkanol ethoxylate; Alkylphenyl ethoxylate; Anionic surfactants → Soaps; Sulfated oils and alkyl sulfates; Alkyl benzene sulfonates; Triethane (Trichlorethylene and perchlorethylene)
  - Pickling
    - Sodium chloride
    - Sulfuric acid

TABLE 11 (Continued)

- Tanhouse Process
  - Chrome Tanning
    - Sodium dichromate
    - Sulfuric acid
    - Glucose or sulfur dioxide
    - Chromium sulfate (basic)
    - Borax
    - Nonionic and cationic surfactants
      - Alkanol ethoxylate
      - Alkylphenyl ethoxylate
      - Cetyl dimethyl benzyl ammonium chloride
    - Sodium bichromate
    - Oxalic acid
    - Sodium carbonate
    - Sodium hydroxide
    - Potassium hydroxide
    - Sodium acetate, diacetate
    - Potassium acetate
    - Sodium bicarbonate
  - Vegetable Tanning
    - Tannins
      - Barks
        - Wattle, etc.
      - Wood
        - Quebracho, etc.
      - Fruits
      - Leaves
      - Roots
    - Syntans
      - Condensation products of formaldehyde and:
        - Naphthalenesulfonic acids
        - Phenols and sulfonate phenols
        - Diaryl sulfones
        - Urea
        - Melamine
        - Dicyandiamide
      - Nonformaldehyde condensed from materials such as:
        - Styrenemaleic anhydride
        - Aryl diisocyanates
        - Ligninsulfonates
    - Anionic Surfactants
      - Soaps
      - Sulfated oils and alkyl sulfates
      - Alkyl benzene sulfonates

TABLE 11 (Continued)

- Retan, color, fatliquor process
  - Retan
    - Vegetable tanning process for chrome tanned hides
  - Color
    - Formic acid
    - Syntans → naphthalene and phenolic synthetic
    - All kinds of surfactants
    - Hydrogen peroxide
    - Sodium sulfide
    - Hydrochloric acid
    - Titanium dioxide
    - Ammonium bicarbonate
    - Dye (coal tar)
      - Acid dyes
      - Metallized dyes
      - Mordant dyes
      - Direct dyes
      - Developed dyes
  - Fatliquor, Oiling, Stuffing
    - All kinds of surfactants
    - Oils
      - Neatsfoot
      - Cod
      - Sperm
      - Castor
      - Coconut
      - Palm
      - Wool grease

TABLE 11 (Continued)

- Finishing Process
  - Impregnation
    - Aqueous emulsions of acrylic copolymers - Primal Emulsions (e.g.)
    - Anionic or nonionic surfactants
  - Patent leathers
    - Naphtha
    - Boiled linseed oil
  - Water or oil repellent
    - Stearato chromic chloride complex
    - Chrome complexes of perfluro fatty acids
    - Chlorinated hydrocarbons
      - Triethane (e.g.) (1,1,1 trichloroethane and trichloroethylene)
  - Solvents for
    - Dyestuffs
    - Resins
    - Oils
    - Lacquers
    - Varnishes
      - Alcohols
      - Polyols
      - Glycol - ethers
      - Esters and ethers
      - Ketones
  - Nitrocellulose lacquers
  - Pigments in water solution containing some hardening protein such as shellac or albumin
    - 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

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 $\simeq 40\ ft^2$ of leather (3.72 sq.m).
$\sim 25 \times 10^6$ hides to be tanned in 1976
($\sim 22 \times 10^6$ hides tanned in 1975)

$$\left(\frac{25 \times 10^6 \text{ hides}}{\text{year}}\right)\left(\frac{50 \text{ lb}}{\text{hide}}\right) = \frac{1.25 \times 10^9 \text{ lb}}{\text{year}}$$

$$\left(\frac{0.35 \text{ lb collagen}}{\text{lb}}\right)\left(\frac{1.25 \times 10^9 \text{ lb}}{\text{hide}}\right)(0.88)^* = \frac{385 \times 10^6 \text{ lb collagen}}{\text{year}}$$

$$\left(\frac{0.06 \text{ lb chrome oxide fixed}}{\text{lb collagen}}\right)\left(\frac{385 \times 10^6 \text{ lb collagen}}{\text{year}}\right) = \frac{22 \times 10^6 \text{ lb chrome oxide fixed}}{\text{year}}$$

$$\frac{23 \times 10^6 \text{ lb chrome oxide/year}}{\text{(0.7 of total used is fixed)}} = \frac{33 \times 10^6 \text{ lb chrome oxide required}}{\text{year}}$$

(~10 million lb lost/yr)
(4.55 million kg)

Dyes (Calculated by two different methods)

A. Based on estimated dollar value of dye market
(Source: Personal communication with representative of dye manufacturers)

Basis: Value of dyes sold $\simeq 15 \times 10^6$/year
Average price of \$3/lb (6.60/kg)
Consumption range 5×10^6 lb/year
Estimated sales distribution

Acid dyes	\$9 million
Direct dyes	\$3.7 million
Basic dyes	\$1 million
Solvent dyes	\$1 million
Sulfur dyes	\$0.1 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:

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

Dye loss to sewer may range from 1.1 to 2.8×10^6 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.

	Unit Operation	Waste Product Liquid	Waste Product Solid
Beamhouse Process	Siding and trimming	X	X
	Washing & soaking	X	X
	Fleshing	X	X
	Unhairing	X	X
Tanhouse Process	Bating	X	
	Pickling	X	
	Tanning	X	X
	Splitting		
Retan, Color, Fat-liquor Process	Retan	X	X
	Bleaching	X	
	Coloring	X	X
	Fatliquoring	X	
Finishing Process	Drying, wet-in coating tacking, etc.	X	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

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

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

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

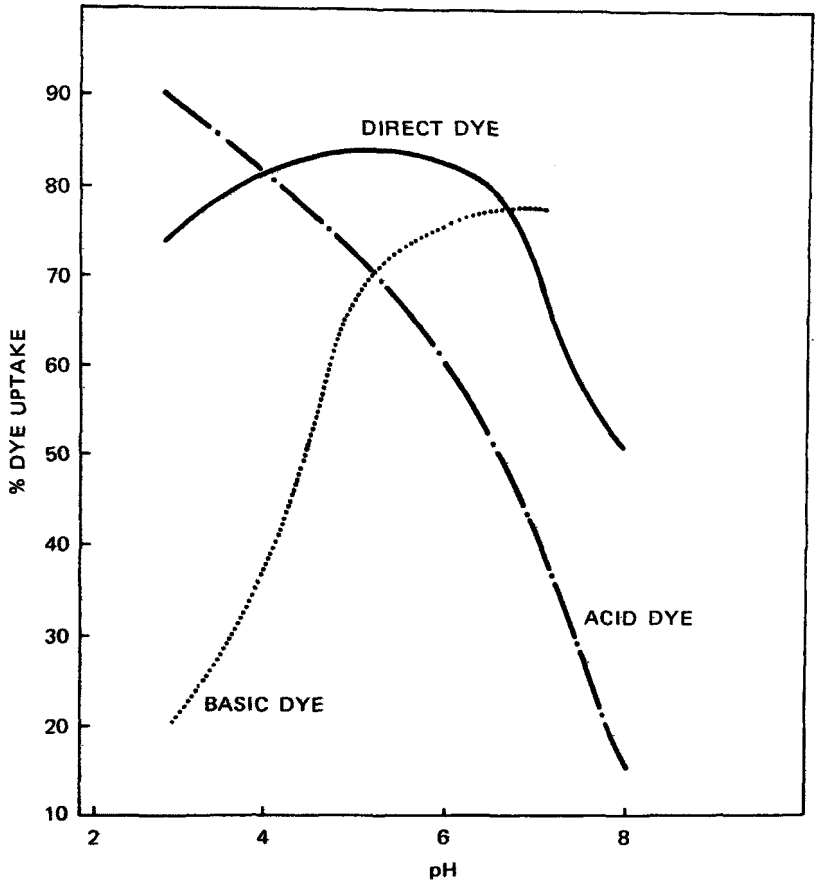
DATA ACQUISITION

An extensive literature search was made to collect information on dyeing of leather, but this resulted in little data. Therefore, on-site visits were deemed necessary. Visits were made to four tanneries, which 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/lb 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. From all sources, it is apparent that dye formulations 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 of dye used depends on the color, the type of leather (split, or grain, cattle, sheep, or other), and even the mix of dyes. Mixtures of dyes are often used to obtain a specific color. The uptake of dye by the leather also depends on the color desired. Cycle times are from 4 to 8 hours and only estimates are available on actual dye



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

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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.

TABLE 13. SURVEY OF THE LEATHER INDUSTRY TANNERY

	Tannery			
	A	B	C	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 average range)				
Float	2-3/1	~4/1	1-2/1	1-2/1
Dye/kg of leather (wet)	Δ	typical 6 kg/900 kg or 0.7%	0.25 - 5%	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	~1 mgd total to municipal sewer	No data - directly to municipal sewer	20 to 40 BOD except when t < 20°F; then BOD can go up to 200 under severe winter conditions
Products	Garment & shoe leather	Chrome tanned upholstery 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

? = 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.

Δ 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 1.61×10^6 ℓ/day (~ 58.2 ℓ/kg of 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 1.14×10^6 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

TABLE 14. ESTIMATED EFFLUENT STREAM LOAD FROM A 1000 CATTLE HIDE/DAY TANNERY (60 LB GREEN SALTED CATTLE HIDE)

Processing Steps	Flow (10^3 ℓ/day)	BOD (kg/day)	Total suspended solids (kg/day)	Total solids (kg/day)	Oil and grease (kg/day)	Sulfide (kg/day)	Chromium (kg/day)	pH
Soaking	189	409	682	5,864	--	--	--	6.0-8.0
Unhairing	189	1,364	1,773	4,090	273	205	--	11.0-12.5
Liming	379	273	409	1,364	136	273	--	11.0-12.5
Bating	227	22.7	191	545	545	--	--	7.0-10.0
Chrome tanning	57	10.9	136	4,090	273	--	136	3.5-4.0
Retan, coloring and fatliquoring	379	54.5	81.8	545	45.5	--	27.3	4.0-5.0
Finishing	189	81.8	136	218	273	--	--	5.0-8.0

Source: Thorstensen, T. C., "Practical Leather Technology", R. E. Krieger Publishing Company, Huntington, New York, 1976, p. 263.

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 1.14×10^6 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_5 measurements of unfiltered samples. Much of the BOD_5 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 = 2
Average dye used per hide (0.7% of a 50# hide)	= 0.35 lb

Range of Uptake

Dye Required

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

Upper Limit of Dye Fixed

(Dye required, lb) $\left\{\begin{array}{l}\text{Uptake of 75\% for 10\% of hides}\\ \text{Uptake of 85\% for 90\% of hides}\end{array}\right\}$ Range of dye fixed at upper limit

$$(7.00 \times 10^6)(0.75)(0.10) = 0.53 \times 10^6$$

$$(7.00 \times 10^6)(0.85)(0.90) = 5.36 \times 10^6 \text{ lb}$$

$$= 5.89 \times 10^6 \text{ lb fixed total}$$

Lower Limit of Dye Fixed

$$(7.00 \times 10^6)\ (0.60) = 4.2 \times 10^6 \text{ lb fixed}$$

$$\text{Dye Loss Range} = (7.00 \times 10^6 - 5.89 \times 10^6) \text{ to } (7.00 \times 10^6 - 4.2 \times 10^6)$$

$$= 1.1 \times 10^6 \text{ to } 2.8 \times 10^6 \text{ lb dye}$$

Overall Industry Wastewater Flow Quantities

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

Concentration Range Based on Average Flow

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

$$\frac{1 \times 10^9 \text{ lb}}{\text{year}} \times \frac{6 \text{ gal}}{\text{lb}} = \frac{6 \times 10^9 \text{ gal}}{\text{year}} \text{ (or } 50 \times 10^9 \text{ lb } H_2O/\text{yr)}$$

TABLE 15. (Continued)

Low Concentration $\frac{1.1 \times 10^6 \text{ lb dye/yr}}{50 \times 10^9 \text{ lb } H_2O/\text{yr}} = 22 \text{ ppm}$

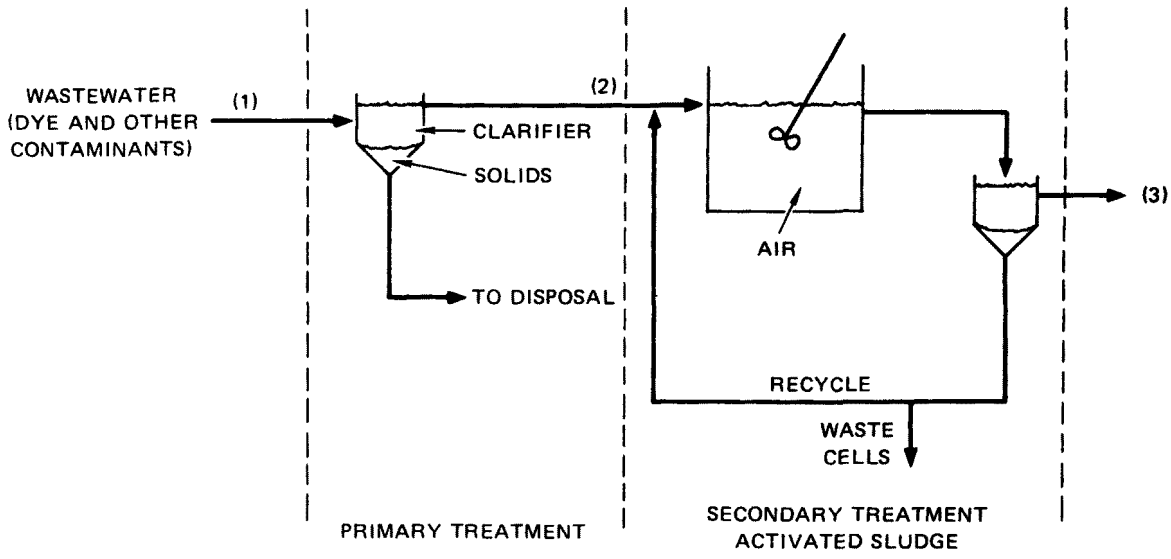
High Concentration $\frac{2.8 \times 10^6 \text{ lb dye/yr}}{50 \times 10^9 \text{ lb } H_2O/\text{yr}} = 56 \text{ ppm}$

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

Low Concentration $\frac{1.1 \times 10^6 \text{ lb}}{\left(\frac{50 \text{ lb}}{\text{hide}}\right)\left(\frac{20 \times 10^6 \text{ hides}}{\text{yr}}\right)\left(\frac{2 \text{ lb } H_2O}{\text{yr}}\right)} = 560 \text{ ppm}$

High Concentration $\frac{2.8 \times 10^6 \text{ lb}}{\left(\frac{50 \text{ lb}}{\text{hide}}\right)\left(\frac{20 \times 10^6 \text{ hides}}{\text{yr}}\right)\left(\frac{2 \text{ lb } H_2O}{\text{yr}}\right)} = 1400 \text{ ppm}$

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.



ESTIMATED STREAM CONCENTRATIONS

	(1)	(2)	(3)
FLOW*, gal/day	300,000		
DYE, mg/l	22-56 {≤112 mg/l OF COD	†	
BOD, mg/l	1,900	1,140 (40%)‡	≥20
COD, mg/l	5,200	3,800 (27%) §	NA
SS, mg/l	2,800	1,430 (49%) §	≥30
TOTAL Cr, mg/l	86	13 (63%) §	—
GREASE, mg/l	380	140 (85%) §	—
SULFIDES, mg/l	190		

*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.

†Since 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.

‡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.

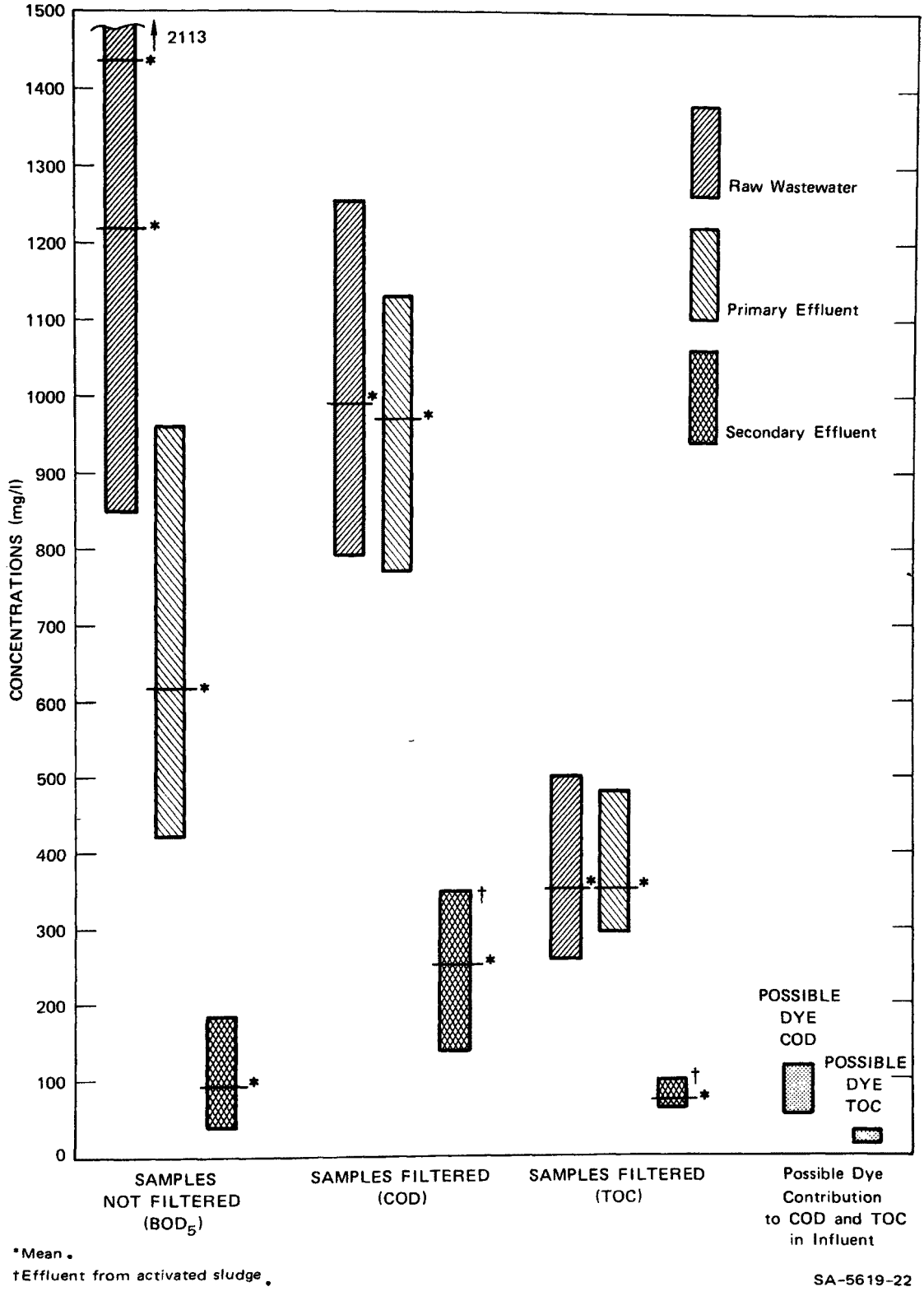


FIGURE 4. ESTIMATES OF BOD_5, COD, AND TOC OF EFFLUENT STREAMS OF TANNERY

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 a 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 maintain a large population of viable microorganisms. Removal of dyes by biosorption (perhaps by reaction with proteinaceous cellular material) may be the major mechanism for removal of the dyes in the activated sludge unit. A similar mechanism may be responsible 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.

SECTION 6

TOXICITY AND ENVIRONMENTAL FATE OF DYES

TOXICITY OF DYES

Because no data are available on the actual extent of removal of dyes in treatment plants (industrial or combined municipal/industrial) 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 in the environment.

Toxicity to Acquatic Organisms

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

The ADMI study showed that the basic dyes are generally more toxic than the acid or direct dyes. Table 16 shows that of 15 basic dyes tested, 13 inhibited the growth of *S. 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 LC50s of less than 1 mg/liter.

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 LC50s 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 LC50s greater than 180 mg/liter. Direct Blacks 38 and 80 inhibited algal growth by at least 80% at 10 mg/liter.

TABLE 16. TOXICITY* OF ACID, BASIC, AND DIRECT DYES TO THE GREEN ALGA, SELENASTRUM CAPRICORNUTUM

Dye	Concentration† producing at least 50% inhibition	Concentration† producing at least 80% inhibition
Acid Black 1	10	>10
Acid Blue 25	10	>10
Acid Blue 113	10	>10
Acid 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
Basic 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

* 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.

TABLE 17. TOXICITY OF ACID, BASIC, AND DIRECT DYES TO THE FATHEAD MINNOW, *PIMEPHALES PROMELAS*

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	125
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

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 be related to chemical structure; however, preliminary inspection of the structures did not reveal any obvious relationships. A more comprehensive evaluation is beyond the scope of this project.

Effluent from the leather industry contains, among other substances, a mixture of dyes. 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 to be acutely toxic to aquatic organisms 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.

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

The log P (octanol-water partition coefficient values) for some azo dyes are relatively high, indicating high lipophilicity and therefore a tendency to bioaccumulate. For azobenzene, 4-aminoazobenzene, 4-dimethylaminoazobenzene, and 2-methyl-4-[(2-methylphenyl)azo] benzenamide, the log P values are 3.82, 3.50, 4.58, and 4.24, respectively. Other nonpolar dyes may have a high bioaccumulation potential also.

Potential Human Health Effects

Few toxicological studies with laboratory mammals have been performed on dyes specific to the leather industry; hence, no positive conclusions can be made concerning the impact of these dyes on human health. However, many of the dyes are aromatic amines, a class of compounds comprising a large number of suspected carcinogens. Other dyes possess diazo groups, which, if cleaved, 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 in the IARC Monograph indicates that Direct Blue 53 may be carcinogenic and teratogenic. Studies have been performed on Acid Red 2 and Acid Orange 20, but the data are inadequate for judging the potential of these dyes to produce cancer.

ENVIRONMENTAL FATE

There are few data on which to base an environmental fate assessment for dyes introduced into waters by the leather industry. This is 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 the aquatic environment. The mixtures of dyes also contain impurities, which adds to the complexity of the assessment.* Additionally, the industry itself has had no facilities for determining the composition of the effluent streams. Most of the dyes used in the leather industry are protein-binding dyes and the waste streams in a tannery containing hair, flesh, trimmings, and other materials are high in protein and could be expected to bind many of the dyes and thus remove them from the stream. This process, however, would probably depend on the pH and chemical composition of the effluent stream.

Physical Properties

No physical properties were available, in part probably because the impurities in dyes themselves make measurements of data questionable. From the general structure of various dyes, some of which 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 ~ 20°C with half-lives of a year or more

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* Ecological and Toxicological Association of the Dyestuff Manufacturing Industry (ETAD), based in Switzerland, apparently has data on the environmental fate of some dyes which may provide information. This information is being sought.

(Mabey and Mill, 1978). Since such reactions are slow, and only affect a minor part of the dye structure, hydrolysis should not be considered an important 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 source, which partially simulates the wavelengths and distribution of the solar spectrum. The photolyses were followed by decreases in absorbance at wavelengths in the visible region. The data were plotted by Porter as (concentration) versus (time); a straight-line plotted in 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). Photolyses were also conducted with the dyes Basic Green 4 and Direct Blue 76 in sunlight. The photolysis data for the sunlight and carbon-arc light experiements are summarized in Table 18.

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

TABLE 18. PHOTOLYSIS OF DYES

		% Reaction after 200 hr with carbon arc lamp*
Basic Dyes		
Basic Violet	3	78
Basic Blue	9	58
Basic Green	1	90
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 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.

† 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 <u>any</u> 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.

TABLE 19. SOME DYES USED IN THE LEATHER INDUSTRY

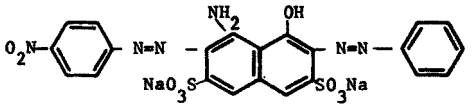
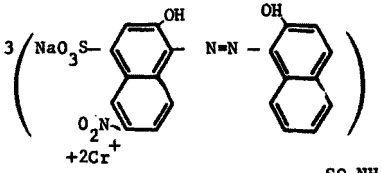
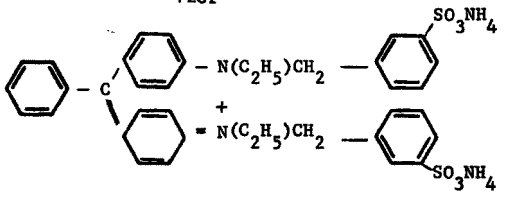
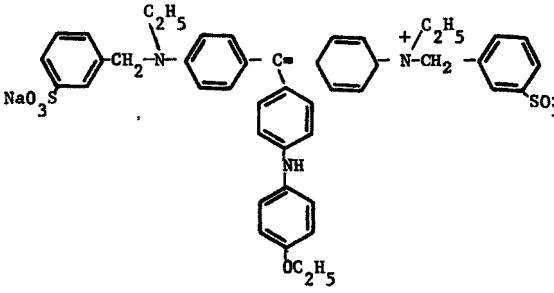
C.I. Name	CAS No.	Structural Formula	Empiral Formula	C.I. No.	Remarks
Acid Black 1	3121-74-2 (Free) 1064-48-8 (Na^+salt)		$C_{22}H_{14}N_6O_9S_2$	20470	
Acid Black 2	8005-03-6; 12227-81-5			50420	Sulfonate of compounds formed by heating nitrobenzene, aniline and aniline hydrochloride with Fe or Cu at 180-200°C or using nitrophenol or nitrocresols instead of nitrobenzene
Acid Black 52	5610-64-0(Na^+salt) Cr^{+++}complex 10279-69-3			15711	2 Cr^{++} to 3 molecules of the monoozodye
Acid Blue 9	2650-18-2 $(NH_4)_2$ salt		$C_{37}H_{43}N_4O_6S_2$	42090	
Acid Blue 83	25305-85-5 6104-59-2(Na salt)		$C_{45}H_{45}N_3O_7S_2$	42660	

TABLE 19. (Continued)

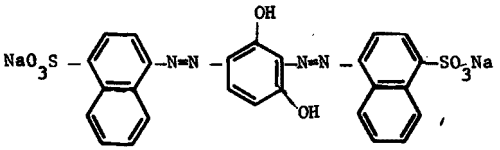
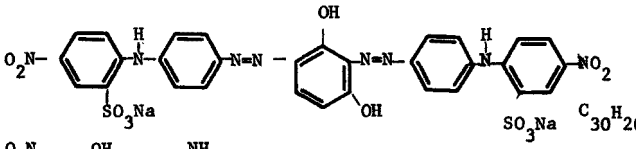
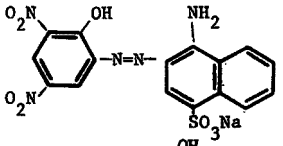
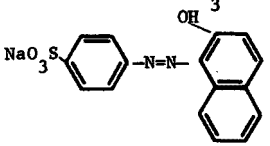
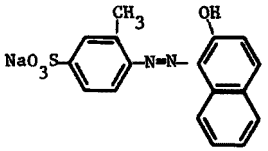
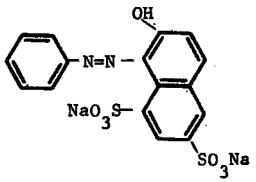
C.I. Name	CAS No.	Structural Formula	Empirical Formula	C.I. No.	Remarks
Acid Brown 14			$C_{26}H_{16}N_4Na_2O_8S_2$	20195	
Acid Brown 354			$C_{30}H_{20}N_6Na_2O_{12}S_2$	20177	
Acid Green 35			$C_{16}H_9N_5NaO_8S$	13361	Cr^{+++} complex is used
Acid Orange 7	573-89-7 (Mono Na salt, 633-96-5)		$C_{16}H_{11}N_2NaO_4S$	15510	
Acid Orange 8	18524-46-4; 5850-86-2		$C_{17}H_{13}N_2NaO_4S$	15575	
Acid Orange 10	1936-15-8		$C_{16}H_{10}N_2Na_2O_7S_2$	16230	

TABLE 19. (Continued)

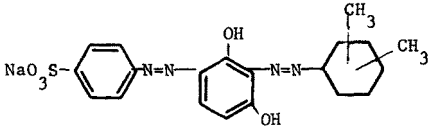
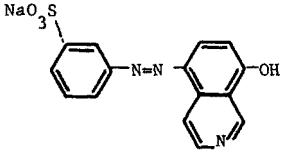
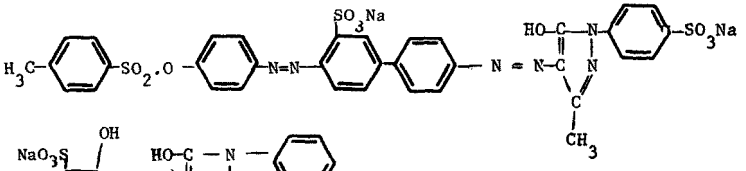
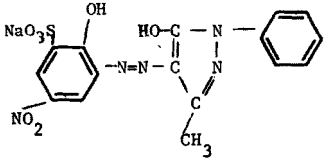
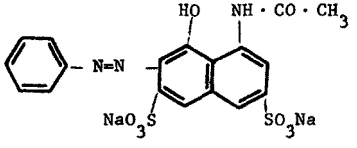
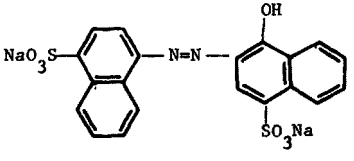
C.I. Name	CAS No.	Structural Formula	Empirical Formula	C.I. No.	Remarks
Acid Orange 24	1320-07-6		$C_{20}H_{17}N_4NaO_5S$	20170	
Acid Orange 61			$C_{15}H_{10}N_3NaO_4S$	19320	CR^{+++} complex is used
Acid Orange 63			$C_{35}H_{26}N_6Na_2O_{10}S_3$	22870	
Acid Orange 74	10127-27-2		$C_{16}H_{11}N_5NaO_6S$	18745	Cr^{+++} complex is used
Acid Red 1	25317-20-8 3734-67-6		$C_{18}H_{13}N_3Na_2O_8S_2$	18050	
Acid Red 14	13613-55-3 3567-69-9		$C_{20}H_{12}N_2Na_2O_7S_2$	14720	

TABLE 19. (Continued)

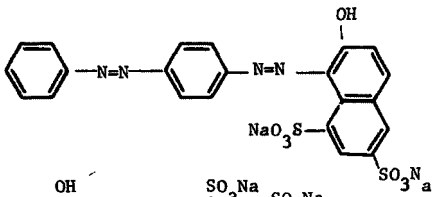
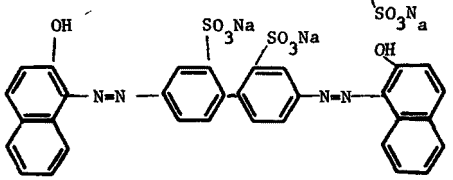
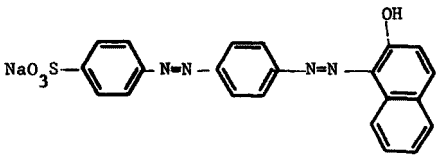
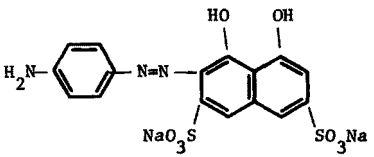
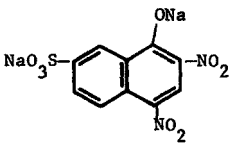
C.I. Name	CAS No.	Structural Formula	Empirical Formula	C.I. No.	Remarks
Acid Red 73	5413-75-2		$C_{22}H_{14}N_4Na_2O_7S_2$	27290	
Acid Red 97			$C_{32}H_{20}N_4Na_2O_8S_2$	22890	
Acid Red 151			$C_{22}H_{15}N_4NaO_4S$	26900	
Acid Violet 3	1681-60-3		$C_{16}H_{11}N_3Na_2O_8S_2$	16580	
Acid Yellow 1			$C_{10}H_4N_2Na_2O_8S$	10316	

TABLE 19. (Continued)

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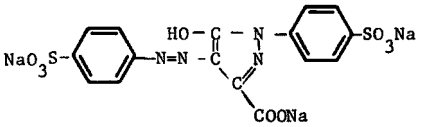
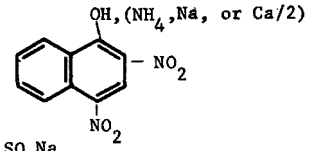
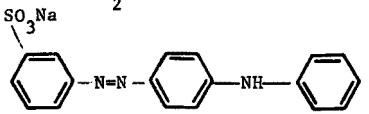
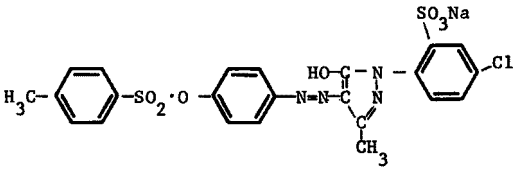
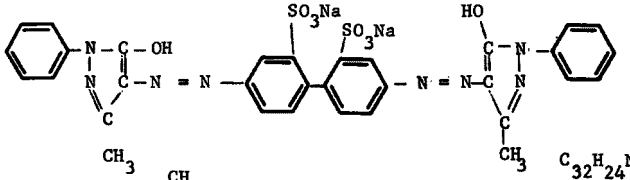
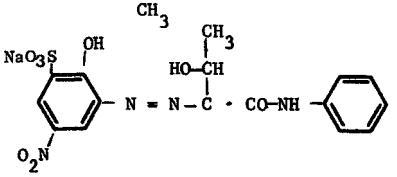
Acid Yellow 23	118-26-3; 1934-21-0; 34175-08-1		$C_{16}H_9N_4Na_3O_9S_2$	19140	
Acid Yellow 24	605-69-6; 887-79-6; 10142-54-8		$C_{10}H_6N_2O_5$ (or $C_{10}H_5N_2O_5 \cdot NH_4$, Na, or Ca/2)	10315	
Acid Yellow 36	4005-68-9; 587-98-4		$C_{18}H_{14}N_3NaO_3S$	13065	
Acid Yellow 40	6372-96-9		$C_{22}H_{18}ClN_4NaO_7S_2$	18950	
Acid Yellow 42	24382-22-7		$C_{32}H_{24}N_8Na_2O_8S_2$	22910	
Acid Yellow 99	10343-58-5		$C_{16}H_{13}N_4NaO_8S$	13900	Cr^{+++} complex used

TABLE 19. (Continued)

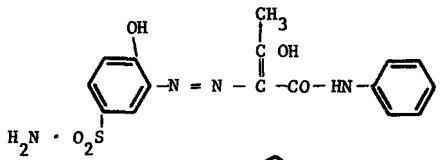
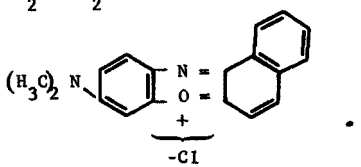
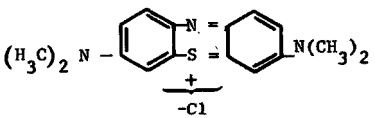
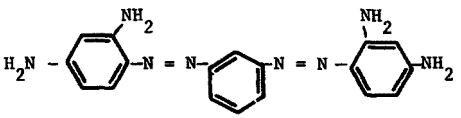
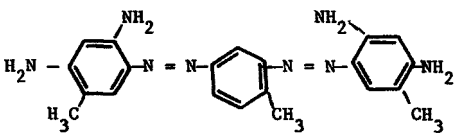
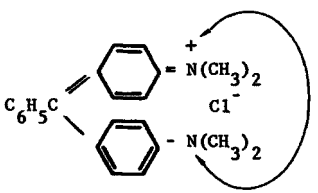
C. I. Name	CAS No.	Structural Formula	Empirical Formula	C.I. No.	Remarks
Acid Yellow 151	12715-61-6		$C_{16}H_{16}N_4O_5S$	13906	
Basic Blue 6	7057-57-0		$C_{18}H_{13}ClN_2O$	51175	Zinc double chloride complex
Basic Blue 9 (Methylene blue)	61-73-4		$C_{16}H_{18}ClN_3S$	52015	
Basic Brown 1	1052-38-6		$C_{18}H_{18}N_8$	21010	
Basic Brown 4	4482-25-1		$C_{15}H_{24}N_8$	21010	
Basic Green 4 (Malachite Green)	569-64-2		$C_{23}H_{19}ClN_2$	42000	

TABLE 19. (Continued)

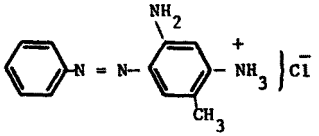
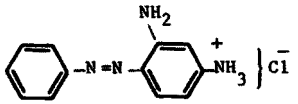
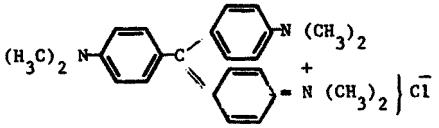
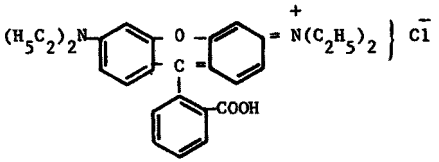
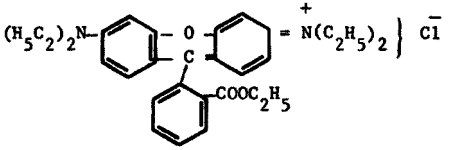
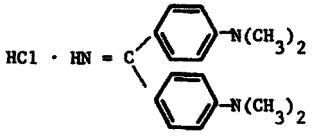
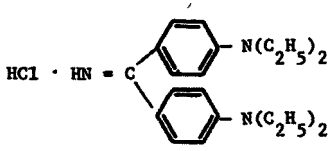
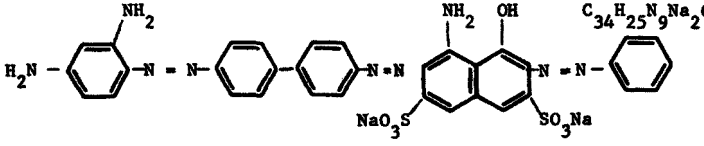
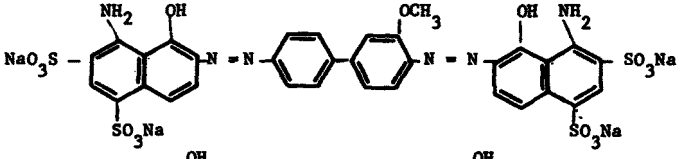
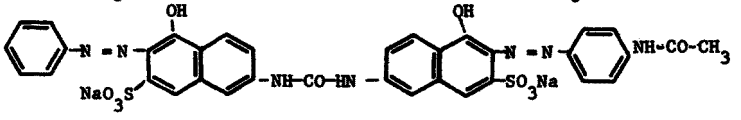
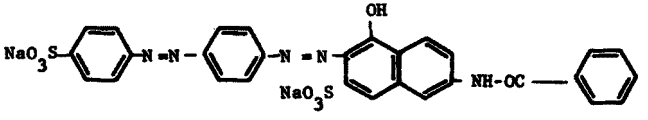
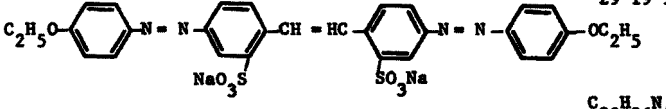
C.I. Name	CAS No.	Structural Formula	Empirical Formula	C.I. No.	Remarks
Basic Orange 1	5042-54-6 4438-16-8		$C_{13}H_{15}ClN_4$	11320	
Basic Orange 2 (Chrysoidine)	495-54-5; 532-82-1		$C_{12}H_{13}ClN_4$	11270	
Basic Violet 1 (Methyl violet)	8004-87-3			42535	
Basic Violet 3 (Crystal violet)	548-62-9		$C_{25}H_{30}ClN_3$	42555	
Basic Violet 10	81-88-9		$C_{28}H_{31}ClN_2O_3$	45170	
Basic Violet 11	2390-63-8		$C_{30}H_{35}ClN_2O_3$	45175	

TABLE 19. (Continued)

C.I. Name	CAS No.	Structural Formula	Empirical Formula	C.I. No.	Remarks
Basic Yellow 2	2465-27-2		$C_{17}H_{22}ClN_3$	41000	
Basic Yellow 37	6358-36-7		$C_{19}H_{30}ClN_3$	41001	
Direct Black 38	1937-37-7		$C_{34}H_{25}N_9Na_2O_7S_2$	30235	
Direct Blue 1	2610-05-1		$C_{33}H_{22}N_6Na_4O_{15}S_4$	24410	
Direct Red 23	3441-14-3		$C_{35}H_{25}N_7Na_2O_{10}S_2$	29160	
Direct Red 81	2610-11-9		$C_{29}H_{19}N_5Na_2O_8S_2$	28160	
Direct Yellow 12	2870-32-8		$C_{30}H_{26}N_4Na_2O_8S_2$	24895	

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 azo and/or nitro functions. Their colors are attributed to the characteristics of the conjugated unsaturated structures, and the dyeing characteristics are attributed to the binding capacities of these compounds to the protein in the leather, particularly with the sulfonic acid functions. Proprietary mixtures are frequently 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 staining takes place, it indicates combination of the pigmented product with the protein. This may interfere with the physiological processes of the cell. Fortunately, not all products used in coloring are toxic and some are actually essential for physiological functions; such products include 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 in themselves toxic. Sulfonates such as di-sodium-phenol-tetrabromophthalein disulfonate (Bromsulfalein) have been used in protein analysis because, under acid conditions, they readily precipitate proteins.

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 to the structures of susceptible substrates. If novel substrates are examined for biodegradability or persistence, by aerobic or anaerobic processes, periods of acclimation of a large microbial population are required. These are complex processes that are not adequately understood, but with some relatively simple compounds co-metabolism or diauvic growth phenomena have been observed. Even under seemingly oxidative conditions, reductive processes such as the transformations of $R\text{-}NO_2$ to $R\text{-}NH_2$ 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

in the leather tanning industry are decomposed, the nitro and azo functions are reduced to finally yield amino compounds. These amino compounds are then deaminated to form ammonium ions and the nitrogen is finally oxidized to nitrate. Aromatic nuclei are oxidized to catechols and the ring structures are subsequently ruptured to yield products that are generally more readily metabolized.

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

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

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

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

inhibition of digestion was observed only with sewage-dye-activated-sludge. In the same publication, Etzel and Grady (1973) reported that two anthraquinone dyes had strong enough activity to cause failures in laboratory scale anaerobic digesters. The concentration of dye added was 150 mg/liter . The dispersing agent Tamo-SN also had a similar acute effect. Other dyes showed some effects, but these were not sufficiently serious to cause disruption of the anaerobic processes. Decolorization was observed 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 dyes and the problems of the application of such adsorption processes to tannery-plant effluents containing other products that interfere with color removal. If tannery effluents with dye are highly diluted with municipal wastewaters, it is possible that they are eliminated by adsorption on activated sludge and may escape attention because of this high dilution.

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

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16. ABSTRACT

This study focused on the organic dyes released to the environment in the wastewaters from leather dyeing operations. Basically, three types of dyes--acid, basic, and direct--are 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 sewers. 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 environment. 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 DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Industrial Wastes, Wastewater, Toxicity, Organic Compounds, Dyeing	Leather Tanning	13B

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