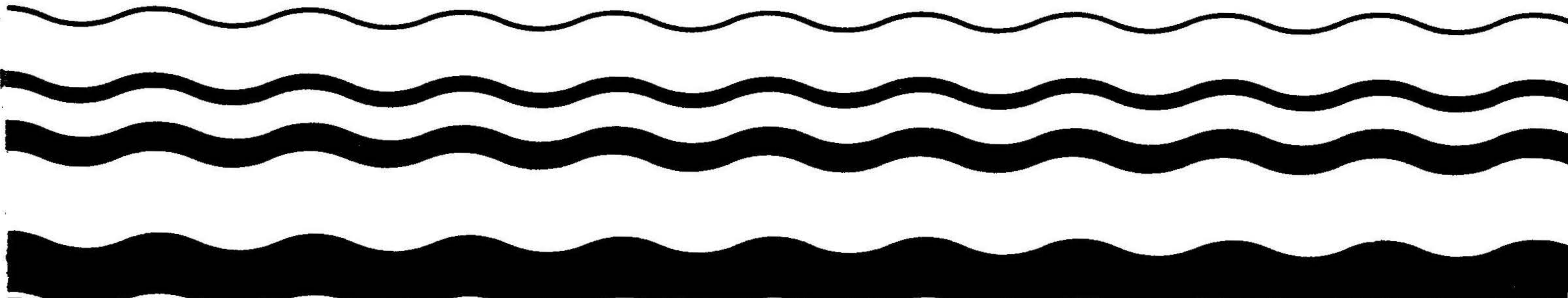


Water and Waste Management



Guidance Document for the Control of Water Pollution in the :

Photographic Processing Industry



GUIDANCE DOCUMENT
for the
CONTROL OF WATER POLLUTION IN
THE PHOTOGRAPHIC PROCESSING INDUSTRY

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CONTENTS

<u>Section</u>		<u>Page</u>
I	CONCLUSIONS	I-1
II	SUMMARY	II-1
III	CHARACTERISTICS OF THE INDUSTRY AND PROCESSES	III-1
	Industry Description	III-1
	Process Descriptions	III-4
	Black and White Photographic Processing	III-4
	Color Photographic Processing	III-8
	Processing Chemistry	III-12
	Processing Equipment	III-34
	In-Process Control Technologies	III-37
	Effect of In-Process Controls on Product Quality	III-37
	Silver Recovery	III-39
	Coupler Recovery	III-46
	Bleach Regeneration	III-46
	Developer Regeneration	III-52
	Water Conservation	III-53
	End-of-Pipe Treatment Technologies	III-56
	Industry Characteristics	III-62
IV	INDUSTRY CATEGORIZATION	IV-1
	Introduction	IV-1
	Categorization Basis	IV-1
	Selection of Production Related Parameter	IV-12
V	PROCESS WASTE CHARACTERIZATION	V-1
	Data Base	V-1
	Processes Used	V-9
	Water Use	V-17
	Process Waste	V-19
	Effluent Characteristics	V-25
VI	SELECTION OF POLLUTANT PARAMETERS	VI-1
	Description of Pollutant Parameters of Significance	VI-5

VII	CONTROL AND TREATMENT TECHNOLOGIES . . .	VII-1
	In-Process Control Technologies . . .	VII-1
	End-of-Pipe Treatment Technologies . . .	VII-23
	Variability Factor	VII-27
VIII	COST, ENERGY, WASTE REDUCTION BENEFITS AND NON-WATER ASPECTS OF TREATMENT AND CONTROL TECHNOLOGIES	VIII-1
	Introduction	VIII-1
	General Cost References and Rationale	VIII-1
	Control and Treatment Costs for Representative Photoprocessing Plants	VIII-4
	Non-Water Quality Aspects	VIII-33
IX	ACKNOWLEDGMENTS	IX-1
X	BIBLIOGRAPHY	X-1
XI	GLOSSARY	XI-1
APPENDIX A	- Telephone Contact Survey Memo	A-1
APPENDIX B	- Long-Term Plant Effluent Data	B-1

FIGURES

<u>Number</u>		<u>Page</u>
III-1	Process: black and white negative - film and paper	III-15
III-2	Process: black and white reversal	III-16
III-3	Process: color negative film, Kodak C-22	III-17
III-4	Process: color negative film, C-41 . . .	III-18
III-5	Process: color negative film, Kodak MC-42	III-19
III-6	Process: color negative film, ECP-1, ECN-1, ECP-2	III-20
III-7	Process: color negative film, ECN-2 . . .	III-21
III-8	Process: color reversal film (IC), E-3 .	III-22
III-9	Process: color reversal film (IC), EM-25, E-4, ME-4, ECO-3, CRI-1	III-23
III-10	Process: color reversal film (IC), E-7M	III-24
III-11	Process: color reversal film (IC), E-6	III-25
III-12	Process: color reversal film (DC), K-12	III-26
III-13	Process: color reversal film, (DC), K-14	III-27
III-14	Process: color negative paper, EP-2 . . .	III-28
III-15	Process: color negative paper, EP-3, 85/86	III-29

III-16	Process: color negative paper, MC-111 . . .	III-30
III-17	Process: color reversal paper, EPR-5, EPR-100	III-31
III-18	Process: color reversal paper, P-10 . . .	III-32
III-19	Process: color reversal paper, P-18 . . .	III-33
IV-1	Process water use vs. production	IV-5
IV-2	Amount of silver in effluent vs. production	IV-6
IV-3	Age of plant vs. process water use . . .	IV-7
IV-4	Age of plant vs. amount of silver in effluent	IV-8
IV-5	Number of employees vs. process water use	IV-9
IV-6	Number of employees vs. amount of silver in effluent	IV-10
VII-1	Total cyanide content in effluent - no bleach regeneration	VII-6
VII-2	Total cyanide content in effluent - plant using bleach regeneration	VII-7
VII-3	Total cyanide content in effluent - bleach regeneration and ferrous sulfate precipitation	VII-8
VII-4	Silver content in effluent - no silver recovery on some fix solutions	VII-13
VII-5	Silver content in effluent - silver recovery on all waste fix	VII-14
VII-6	Silver content in effluent - waste fix not in sample	VII-15

VII-7	Effluent silver concentration vs. effluent silver amount	VII-19
VII-8	Cyanide concentration vs. percent production using ferricyanide bleach . .	VII-20
VII-9	Process water elimination schematic . . .	VII-28
VII-10	Long-Term Silver Concentration in Effluent at Plant 6208	VII-31
VIII-1	Silver recovery capital investment costs vs. production	VIII-10
VIII-2	Silver recovery operating costs vs. production	VIII-12
VIII-3	Reverse osmosis equipment capital investment cost vs. flow, includes reverse osmosis, conductivity control and prefilter	VIII-16
VIII-4	Fe EDTA bleach regeneration invested capital costs vs. production	VIII-18
VIII-5	Fe EDTA bleach regeneration operating costs vs. production	VIII-19

TABLES

<u>Number</u>		<u>Page</u>
III-1	Photographic Processing Establishment Categories	III-2
III-2	Number of Plants and Production Breakdown by Size Category	III-3
III-3	Common Color Materials	III-9
III-4	Summary of Kodak "200" Plant Survey . . .	III-64
III-5	Correlation of Type of Service with Production and Water Use from Telephone Survey Information	III-66
III-6	Correlation of Production with Water Use from Telephone Survey Information . . .	III-67
III-7	Correlation of Process Type with Production from Telephone Survey Information . . .	III-68
III-8	Correlation of Processing Methods with Production from Telephone Survey Information	III-69
III-9	Correlation of Replenishment Use with Production from Telephone Survey Information	III-70
III-10	Correlation of Squeegee Use with Production from Telephone Survey Information . . .	III-71
III-11	Correlation of Silver Recovery Use with Production from Telephone Survey Information	III-72
III-12	Correlation of Silver Recovery Methods with Production from Telephone Survey Information	III-73

III-13	Correlation of Bleach Regeneration Use with Production from Telephone Survey Information	III-74
III-14	Correlation of Treatment Use with Production from Telephone Survey Information	III-75
III-15	Correlation of Discharge Method with Production from Telephone Survey Information	III-76
IV-1	Distinguishing Process Characteristics of Various Material Types	IV-3
V-1	Production Summary	V-3
V-2	Photographic Processes Used at Plants Studied	V-10
V-3	Recovery and Regeneration at Plants Studied	V-14
V-4	Estimated Water Use for Plants in the Photoprocessing Industry	V-20
V-5	Processing Machine Tank Overflow Composition Without Application of In-Process Controls - Pollutant Concentration	V-26
V-6	Processing Machine Tank Overflow Without Application of In-Process Controls - Pollutant Amount	V-27
V-7	Before and After Results of Various Silver Recovery Operations	V-29
V-8	Effluent Characteristics with Application of Controls - Concentration	V-30
V-9	Effluent Characteristics with Application of Controls - Pollutant Amounts	V-34

18



V-10	Treatment Technologies Used by Photo-processors Surveyed	V-39
V-11	Sampling of In-Process Controls and End-of-Pipe Treatments	V-40
V-12	Effluent Characteristics After Application of End-of-Pipe Treatments - Pollutant Concentrations	V-41
V-13	Effluent Characteristics After Application of End-of-Pipe Treatments - Pollutant Amounts	V-42
VI-1	Toxic Pollutants	VI-2
VI-2	Conventional Pollutants	VI-3
VI-3	Non-Conventional Pollutants	VI-4
VI-4	Pollutants Found in Significant Quantities in Effluents from Photographic Processing Plants	VI-5
VII-1	Estimated Breakdown of In-Process Control and Treatment Use by Plant Size (Daily Production)	VII-2
VII-2	Total Cyanide Content in Plant Effluent of Plants Using Ferricyanide Bleach with no Regeneration	VII-4
VII-3	Total Cyanide Content in Effluent of Plants Using Ferricyanide Bleach Regeneration	VII-5
VII-4	Total Cyanide Content in Effluent of Plants Using Ferricyanide Bleach Regeneration plus FeSO_4 Precipitation Treatment on Waste Fix	VII-5
VII-5	Results of Silver Recovery on Silver Content in Plant Effluent - No Silver Recovery on Some Processes	VII-10

VII-6	Results of Silver Recovery on Silver Content in Plant Effluent - Silver Recovery on All Processes	VII-11
VII-7	Results of Silver Recovery on Silver Content in Plant Effluent - Silver Recovery on All Waste Fix But Waste Fix <u>Not</u> in Sample	VII-12
VII-8	Results of Silver Recovery on Silver Content in Plant Effluent - Conventional Silver Recovery on All Waste Fix plus Additional Recovery	VII-16
VII-9	Effectiveness of Various Silver Recovery Procedures	VII-17
VII-10	Summary of Prewash Results	VII-21
VII-11	Effect of Countercurrent Washing and Wash Water Recycle on Effluent Hydraulic Loads	VII-23
VII-12	Pollutant Variability Factors	VII-30
VIII-1	Production Categories	VIII-5
VIII-2	Costs for Silver Recovery of Silver from Fix Solutions Using Conventional Methods	VIII-7
VIII-3	Costs for Recovery of Silver from After-Fix Wash Waters by Ion Exchange	VIII-8
VIII-4	Costs for Recovery of Silver from After-Fix Wash Waters by Reverse Osmosis and Precipitation	VIII-9
VIII-5	Costs for Ferric EDTA Bleach Regeneration By Aeration and Chemical Addition . . .	VIII-20
VIII-6	Costs for Ferricyanide Bleach Regeneration By Ozonation	VIII-23

VIII-7	Costs for Ferrous Sulfate Precipitation of Ferricyanide from Waste Fix	VIII-25
VIII-8	Costs for Reduction of Process Wastewater to a Mimimum By Conventional and Advanced Controls Plus Multi-Stage Evaporation	VIII-27
VIII-9	Control and Treatment Costs for Hexavalent Chromium Reduction - Batch Treatment . .	VIII-29
VIII-10	Control and Treatment Costs for Hexavalent Chromium Reduction - Continuous Treatment	VIII-30
VIII-11	Control and Treatment Costs for pH Adjustment (Chromium Treatment)	VIII-31
VIII-12	Control and Treatment Costs for Diatomaceous Earth Filtration (Chromium Treatment)	VIII-32

SECTION I

CONCLUSIONS

This guidance document is the result of a study of the photographic processing industry by the Effluent Guidelines Division of the Environmental Protection Agency. The purpose of the document is to assist local authorities and other interested parties in the control of wastewater pollutants from photographic processing facilities where required. The toxic pollutants of concern which may be present in the raw wastewater are silver, cyanide, and chromium. Silver is present in the raw waste in all facilities and cyanide is present in the raw wastewater in many color processing facilities. Chromium is present in only those facilities which use dichromate bleach. The use of this bleach is generally restricted to some processors of commercial movie film.

Conventional silver recovery (consisting of metallic replacement or electrolytic or both) and ferricyanide bleach regeneration are widely practiced as in-process controls by most of the industry because of economic benefits. Recovery of silver from wash water using ion exchange or reverse osmosis are advanced controls not widely used, although the use of ion exchange is increasing. The use of various in-process controls and treatments by the industry is estimated in Table I-1.

TABLE I-1
ESTIMATED BREAKDOWN OF IN-PROCESS CONTROL AND TREATMENT USE
BY PLANT SIZE (DAILY PRODUCTION)

PERCENTAGE OF PLANTS USING INDICATED CONTROLS BY SIZE
CATEGORY

Pro- duction sq m/ day	Conven- tional Silver Recovery	Ion Exchange	Reverse Osmosis	Ferri- cyanide Bleach Regen- eration	Ferrous Sulfate Precipi- tation	Di- chromat Treat- ment
<93	*	0	0	*	0	0
93-186	95	2	0	50	0	0
186-464	100	8	0	60	0.3	0
464-4,640	100	2	0	90	3	0
over 4,640	100	20	33	95	20	0

* Insufficient information to make reasonable estimate.

These controls reduce the waste loads of silver and cyanide by up to 85 percent. It was also established that more than 99 percent of the photographic processing facilities are indirect dischargers to publicly owned treatment works (POTW) and less than one percent of the facilities have a direct discharge.

Based on the information presented in Section VII, it has been demonstrated that photographic processing facilities can achieve the effluent levels using the indicated in-process control and end-of-pipe treatment technologies described in this guidance document. To determine the 30-day average and single-day maximum silver values, the plant data mean was multiplied by the appropriate variability factors listed in Table VII-12. In the case of total cyanide, the computed single-day variability factor of 12 is inordinately high. A large number of cyanide values were reported which were at the detection limit of the analytical procedures used (0.005 mg/liter). This caused the distribution of data to be badly skewed and resulted in the high variability factor. For this reason the

variability factors for total cyanide were calculated using the individual plant data given in Table VII-4. The calculated total cyanide variability factors at a 99 percent confidence level are 3.7 for the single-day maximum and 1.2 for the 30-day average maximum (see Table VII-12).

Chromium is used in bleach formulations for one color print film and for black and white reversal motion picture films. No known plants in the photographic processing industry using these processes treat their wastewater for the specific reduction of total chromium, and therefore no chromium data from treated effluent were available. The total chromium variability factors determined for the metal finishing industry are used to determine the 30-day and single-day maximum limits. These factors are 1.43 and 4.94, respectively. The average total chromium concentration in the effluents from all plants studied in the metal finishing industry was 0.57 mg/liter after treatment consisting of chromium reduction, chemical precipitation, and clarification. The addition of filtration reduced the effluent chromium level to 0.32 mg/liter. The pollutant amounts were calculated using these concentrations and the average hydraulic load of 157,000 liters/1,000 sq m (3,850 gal/1,000 sq ft) for the photographic processing industry. It is recommended that the after dichromate bleach wash water and waste dichromate bleach be segregated and treated separately from other wastewaters. This reduces the volume of wastewater that must be treated and reduces potential interferences from other photoprocessing chemicals.

The following toxic pollutant levels are given in the form of amount of pollutant per unit of production. Concentration levels are also given for informational purposes. The Agency does not recommend the use of concentration based limitations for controlling pollutants at facilities in the industry. There is, as shown in Section VII, a poor relationship between concentration and the amount of pollutant discharged. The Agency encourages the reduction of wastewater quantities by various water saving controls. Concentration limitations for this industry tend to discourage water use reductions. The silver concentrations given below were calculated from the production normalized amounts and the average production normalized hydraulic load for the industry. For cyanide and chromium, the production normalizing factor is based on the

amount of material processed using ferricyanide or
dichromate bleach, respectively.

I. Silver Controls

Conventional Silver Recovery

	<u>Variability Factor</u>	<u>Effluent Silver Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (from Table VII-6)		0.14 (0.029)	0.90
30-day average maximum	1.3	0.19 (0.038)	1.1
Single-day maximum	4.2	0.59 (0.12)	3.7

Conventional Silver Recovery Plus Ion Exchange Treatment of Wash Waters

	<u>Variability Factor</u>	<u>Effluent Silver Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (from Table VII-8)		0.048 (0.0098)	0.31
30-day average maximum	1.3	0.062 (0.013)	0.40
Single-day maximum	4.2	0.20 (0.041)	1.31

Conventional Silver Recovery plus Reverse Osmosis Treatment of Wash Water and Precipitation of Silver from Concentrate

	<u>Variability Factor</u>	<u>Effluent Silver Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (from Table VII-8)		0.0088 (0.0018)	0.06
30-day average maximum	1.3	0.011 (0.0023)	0.07
Single-day maximum	4.2	0.037 (0.0076)	0.24

L-6
18

II. Cyanide Controls

Ozone Regeneration of Ferricyanide Bleach

	<u>Variability Factor</u>	<u>Effluent Total Cyanide Amount, kg/1,000 sq m (lb/1,000 sq ft)*</u>	<u>Concentration Range,** mg/liter</u>
Plant data mean (from Table VII-3)		4.8 (0.98)	0.4-1.4
30-day average maximum	1.2	7.3 (1.2)	
Single-day maximum	3.7	24 (3.6)	

Ozone Regeneration of Ferricyanide Bleach plus Ferrous Sulfate Precipitation Treatment on Waste Fix

	<u>Variability Factor</u>	<u>Effluent Total Cyanide Amount, kg/1,000 sq m (lb/1,000 sq ft)*</u>	<u>Concentration Range,*** mg/liter</u>
Plant data mean (from Table VII-4)		1.1 (0.23)	0.7-10
30-day average maximum	1.2	1.7 (0.28)	
Single-day maximum	3.7	5.9 (0.85)	

* Based on amount of material processed with ferricyanide bleach.

** The plants exhibiting this concentration range have a ferricyanide bleach production range of 0.3 to 15 percent of the total production.

*** The plants exhibiting this concentration range have a ferricyanide bleach production range of 4 to 100 percent of the total production.

NOTE: The cyanide concentration in the effluents from plants using ferricyanide bleach may exhibit wide variations related to the ratio of ferricyanide production to the total production.

III. Chromium Controls

Chromium Reduction, Precipitation, and Clarification Treatment of Dichromate Bleach Wastes

	<u>Variability Factor</u>	<u>Effluent Total Chromium Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (see text)		0.088 (0.018)	0.57
30-day average maximum	1.43	0.13 (0.026)	0.82
Single-day maximum	4.94	0.43 (0.089)	2.8

Chromium Reduction, Precipitation, Clarification, and Filtration Treatment of Dichromate Bleach Wastes

	<u>Variability Factor</u>	<u>Effluent Total Chromium Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>	<u>Concentration, mg/liter</u>
Plant data mean (see text)		0.049 (0.010)	0.32
30-day average maximum	1.43	0.070 (0.014)	0.46
Single-day maximum	4.94	0.24 (0.049)	1.6

SECTION II

SUMMARY

The photographic processing industry consists of facilities which process various silver halide sensitized photographic products for external customers. There are approximately 11,000 processing facilities distributed throughout the United States. More than 99 percent of the facilities discharge wastewater to POTW's; less than 20 plants were found that discharge directly to surface waters. The industry is divided into four groups: portrait studios (SIC 7221), commercial studios (SIC 7333), photofinishers (SIC 7395), and movie film processors (SIC 7819). The majority of facilities (about 9,900) process less than 93 sq m (1,000 sq ft) of product per day and account for about 12 percent of the total U.S. production. The emphasis of information gathering during this study was directed to plants with production greater than 93 sq m per day which, as a group, accounts for 1,100 plants and 88 percent of the U.S. production.

Photographic processing consists of treating a silver halide sensitized material with a series of chemical solutions and wash water steps to produce a visible image in black and white or color. There are more than 20 different processes used with variations in the solution chemistry and the sequence of solution treatment. Most facilities process a variety of materials and use more than one process. There was no strong basis for subcategorization of the industry based on process use or any of the other factors considered.

The major sources of process wastewater are from waste chemical solutions and waste wash waters. The toxic pollutants found in significant amounts in the plant raw wastewater are silver, cyanide, and chromium. The silver is contained in the emulsion of all the processed materials and is present in the wastewaters from all facilities. Cyanide and chromium are present in some bleach solutions in the form of ferri-ferrocyanide and dichromate compounds, respectively, and are present in the wastewaters from only those facilities which use these types of bleach. It is recognized that silver and cyanide in wastewaters from

photoprocessing facilities are not in a free ionic state but, rather, the silver is combined with thiosulfate as a silver thiosulfate complex and the cyanide is combined with iron as an iron cyanide complex (ferri-ferrocyanide). Cadmium may also be present in the wastewaters in some facilities. It is present in the emulsion of some photographic materials and appears in the wastewaters of facilities which process these materials. Industry has stated that an effort is being made to eliminate cadmium as a constituent of these materials.

The industry removes up to 85 percent of the silver and cyanide, using conventional in-process controls which recover the silver from waste-fix solutions and regenerate ferricyanide bleach for reuse. Other in-process controls in use include ferric EDTA bleach regeneration and process tank squeegees which result in general waste load reductions. These in-process controls are almost universally used throughout the industry and are primarily for the economic benefit gained from silver recovery and chemical savings.

Advanced in-process controls, consisting of ion exchange or reverse osmosis, countercurrent washing, and wash water recycle, are used by some plants. Ion exchange or reverse osmosis is used for recovery of silver from after-fix wash water which contains approximately 10 percent of the totally available silver. Countercurrent washing and wash water recycle (after ion exchange or reverse osmosis) reduce the overall plant hydraulic load. Although there may be some additional economic benefit from using these advanced controls, the usual purposes are conservation and the environmental benefit. The use of these in-process controls in conjunction with standard silver recovery and ferricyanide regeneration reduces silver and cyanide loads by up to an additional nine percent. Controls involving the recycle or reuse of recovered chemicals are not universally applicable to all processes, products, or plant configurations because of the potential effect on product quality. Ion exchange and reverse osmosis treatment of wash waters represent complex advanced technology and requires careful design, selection and installation of equipment, close operating attention, and proper maintenance to achieve reliable results. These requirements could limit potential applications of this technology.

End-of-pipe wastewater treatments are not widely used in the photographic processing industry. Some plants treat waste fix after silver recovery with ferrous sulfate precipitation and settling to reduce the ferricyanide load prior to discharge. Other treatments such as equalization, neutralization, aeration, ozonation, and filtration are used at some plants for waste load reduction to meet specific locally imposed effluent quality requirements.

The use of dichromate bleach is generally limited to facilities which process movie film and only those facilities will have chromium in their wastewater effluent. There are no known facilities in the photographic processing industry which regenerate dichromate bleach or treat their wastewater to reduce the amount of chromium discharged. One facility uses a replenishment-on-demand system to limit the amount of dichromate bleach used to the minimum amount required by the process. The metal finishing industry has demonstrated that a treatment system, consisting of hexavalent chromium reduction, pH adjustment for chromium precipitation, and filtration, is effective in reducing the amount of chromium discharged.

One photographic processing plant has installed an extensive in-process control and end-of-pipe treatment system to approach zero wastewater discharge. The system includes advanced solution reuse, wash water recycle, countercurrent washes, reverse osmosis, ion exchange, and multi-stage evaporation. The applicability of this system to the entire photographic processing industry appears to be limited. The plant using the system is a very large portrait studio which can control the number and type of products and processes used. The system may not be practical for small and medium plants for economic reasons and for plants with more complex product mixes for technical reasons.

This study included the gathering of information related to the cost of installing and operating the various in-process controls and end-of-pipe treatment technologies. Conventional silver recovery and ferricyanide and ferric EDTA bleach regeneration result in a substantial cost benefit to the facilities using them because of the recovery of raw materials. These recovery operations are an important contributor to the profitability of a facility and are almost universally used in the industry. These costs

were included in this study for the information of those few facilities which do not use these in-process controls. The facilities using advanced in-process controls consisting of silver recovery from wash water, countercurrent washing, and wash water recycle and end-of-pipe treatments consisting of ferricyanide precipitation and wastewater evaporation are doing so for the environmental benefit. There appears to be a net cost benefit for the larger plants which recover silver from wash waters. The remainder of the controls have a negative cost impact.

SECTION III

CHARACTERISTICS OF THE INDUSTRY AND PROCESSES

INDUSTRY DESCRIPTION

The photographic processing point source category consists of photographic processing plants processing silver halide sensitized photographic materials to produce continuous-tone black and white or color negatives, positive transparencies, and prints for delivery to external customers. There are approximately 11,000 such photographic processing facilities in the United States found among businesses in four Bureau of the Census Standard Industrial Classification (SIC) codes.

Facilities primarily engaged in photography for the general public are classified as "Photographic Studios, Portrait" (SIC 7221). Included in this group are portrait photographers and school, home, and transient photographers. Establishments engaged in commercial photography are classified in "Commercial Photography, Art, Graphics, and Related Design" (SIC 7333). Facilities primarily engaged in film developing and print processing for the trade or for the general public are included in "Photofinishing Laboratories" (SIC 7395); those engaged in motion picture film processing are classified in "Services Allied to Motion Picture Production" (SIC 7819). The 1972 Bureau of Census determination of the number of establishments classified by each SIC code is given in Table III-1 along with some additional estimates given in the Wolfman Report.

TABLE III-1
Photographic Processing Establishment Categories

	<u>1972 Census</u>
<u>SIC 7221</u> Photo Studios, Portrait with payroll, oper. entire year	5,466
<u>SIC 7333</u> Commercial Photographic Studios with payroll	2,684
<u>SIC 7395</u> Photofinishing Labs with payroll	1,979
<u>SIC 7819</u> Services Allied to Motion Picture Production, with payroll	855
	<u>Wolfman Report</u>
Major labs (amateur)	600
Professional processing labs	775
School finishers	100

A breakdown of the number of plants and the percentage of total production for five categories of plant size (based on daily production) is shown in Table III-2. The amount of production for each size category is expressed as a percentage of the total U.S. production estimated to be approximately 200 million square meters (2 billion square feet) of processed photographic materials per year. All estimates are based on information collected during this study from various industry sources. The plant size categories and "typical" plant production for each category are used in Section VIII of this report for the development of in-process control and treatment costs.

TABLE III-2

NUMBER OF PLANTS AND PRODUCTION BREAKDOWN BY SIZE CATEGORY

Production sq m/day (sq ft/day)	Production Size Category	Typical Production sq m/day (sq ft/day)	Number of Plants	Percent Total U.S. Production
<93 (1,000)	<A	9.3 (100)	9,900	12
93-186 (1,000-2,000)	A	139 (1,500)	200	4
186-464 (2,000-5,000)	B	325 (3,500)	305	84
464-4,640 (5,000- 50,000)	C	1,390 (15,000)	200	
4,640-∞ (50,000-∞)	D	6,970 (75,000)	15	

PROCESS DESCRIPTIONS

Either a two-step or a single-step procedure is used to produce a positive image of the subject on film or paper. In the two-step procedure a chemical process called the "negative" process is used. The first step consists of producing a negative image on film, called a negative transparency, by exposing it to light from the subject and processing the film with the negative process. The transparency is then used as a light mask in the second step to expose paper or film. This material is processed by essentially the same chemical process used in the first step to produce the desired positive image. The single-step procedure uses a "reversal" chemical process which directly produces a positive image of the subject on the film or paper.

The following are detailed descriptions of these negative and reversal processes.

Black and White Photographic Processing

General

Black and white film or paper consists of a base material or substrate, which is coated with a light-sensitive emulsion. Light sensitivity is imparted by distributing silver halide crystals throughout the emulsion. When the emulsion is exposed to a light image, electrons are ejected from the impacted halide atoms. These "free electrons" are in time trapped by crystal imperfections or other chemicals. The electrons attract positively charged free silver ions in the crystal lattice forming clusters of metallic silver at the trap sites. These clusters of metallic silver, still very small, form a latent image of the original light exposure pattern. During processing, the developer solution causes additional silver to be formed at the cluster sites to the extent that the clusters grow, aggregate, and form a visible image, a process of chemical amplification. The film image then undergoes further chemical treatment to stabilize the image and remove excess chemicals. In the reversal process, the additional step of forming the reversal image is required before stabilization.

Negative Process

The negative process is utilized for producing either a negative or a positive image on film or paper. Three basic chemical processing steps are generally used followed by a clean water wash. These steps consist of development, development stop, and fixing. Often the stop step is omitted, and occasionally an emulsion hardening step is added after the fix.

Develop--

The first processing step is developing in which the silver halide crystals in the gelatin emulsion are bathed in a chemical solution, causing the visible image to form. This chemical solution, the developer, contains four primary ingredients:

- (1) A developing agent, usually an organic aromatic compound [e.g., a mixture of hydroquinone and Metol (p-methylaminophenol) or hydroquinone and Phenidone (1-phenyl-3-pyrazolidone)], whose function is to cause the previously formed latent image to grow by reducing additional silver ions at the silver cluster sites;
- (2) An activator or accelerator, commonly sodium hydroxide, sodium carbonate or borax (sodium tetraborate), whose function is to make the developing agent sufficiently active by pH control;
- (3) A preservative, commonly sodium sulfite or sometimes potassium metabisulfite, whose function is to prevent both oxidation of the developing agent and discoloration of the used developing solution; and
- (4) A restrainer, either inorganic (potassium bromide) or organic (benzotriazole), whose function is to prevent the breakdown of the protective layer surrounding each silver halide grain. This reduces fogging caused by development of the unexposed grains.

Short Stop--

Following the development step, the film is immersed in an acid stop bath which neutralizes and, to some extent, removes the developer absorbed in the emulsion. A dilute solution of a weak acid, e.g., 0.5 percent acetic acid, is usually used.

Fix--

The fix step removes unexposed silver halide by converting it into a soluble complex. The fixer solution contains either sodium or ammonium thiosulfate ("hypo") as the principal ingredient. Usually sodium bisulfite or potassium metabisulfite is added to cause an acid condition in the solution to neutralize any developer contamination. The sodium bisulfite or potassium metabisulfite also acts to prevent oxidation of the thiosulfate.

Harden--

This step serves to check emulsion swelling and raise its melting point, thus allowing a higher temperature to be used for drying. Potash alum (potassium aluminum sulfate) is commonly used as the hardening agent though chrome alum (potassium chromium sulfate) is sometimes used. It is common to add the alum compound to the fix solution so that the fixing and hardening are accomplished in a single step.

Wash--

A water wash is the final solution step. Its purpose is to remove the processing chemicals absorbed in the emulsion or substrate.

Dry--

The final processing step is drying the photographic film or paper in a dust-free atmosphere.

Reversal Process

The reversal process forms a direct positive image on the same material used for the original exposure and is most often used for the production of motion picture films and projection slides. It is common to pre-harden the emulsion in the first processing step because more steps are used in the reversal process which tend to soften the emulsion. The pre-hardening solution contains hardening agents such as formaldehyde or succinaldehyde, an antifoggant (6-nitrobenzimidazole and sodium bromide) and sodium sulfate to retard emulsion swelling. After pre-hardening, a neutralizing bath is used to prevent developer contamination. A typical neutralizing solution contains hydroxylamine sulfate and sodium sulfate. The exposed material is fully developed to a negative using a developer solution similar to that used in the negative process except that a small quantity of thiocyanate is added to aid in dissolving small non-light sensitive silver grains. The film is then washed and the silver negative image removed by bleaching in an acidic permanganate or dichromate solution. A clearing bath (for example, bisulfite) is used to remove the bleaching agent and reaction products, leaving the undeveloped silver halide crystals in the emulsion. The emulsion is then given a uniform light exposure, and the remaining silver halide is developed and fixed to provide the positive image. As an alternative to this procedure, a highly fogging developer or non-selective reducer may be used for the second development.

Certain black and white materials, commonly referred to as reversal products, yield a direct "reversal" (positive) image but are processed by the conventional negative process, i.e., no bleach step is used. This is accomplished by incorporating appropriate chemicals into the emulsion during the manufacturing process. These subsequently produce a reversal image during developing.

Color Photographic Processing

General

Unmodified silver halide emulsions are sensitive only to a limited range of wave lengths, including the blue-violet region of the visible spectrum, ultraviolet, and shorter wave lengths. However, certain organic dyes can be included in the emulsion to extend sensitivity to longer wave lengths through the visible spectrum into the infrared or to make the emulsion sensitive to a particular region of the visible spectrum. Color films have three separate light sensitive emulsion layers, which after inclusion of the appropriate dyes, record an image of the blue light components on one layer, the green light components on another, and the red light components on the third layer.

The commonly used color materials are color negative film, color reversal film, color print film, and color print papers. The three basic processes for the processing of color materials are negative, reversal with couplers in the emulsion (IC), and reversal with coupler in the developers (DC). The commonly used color materials, uses, and process types are given in Table III-3.

TABLE III-3
Common Color Materials

<u>Color Material</u>	<u>Use</u>	<u>Process</u>	<u>Image</u>
negative film	original exposure, intermediate for copying positive trans- parencies	negative	negative
positive print film	positive transparency from negative film	negative	positive
reversal film	original exposure, intermediate	reversal (IC) or reversal (DC)	positive or negative
positive print paper	print from negative film	negative	positive
reversal paper	print from positive transparency	reversal (IC)	positive

Descriptions of these color processes follow. They apply to both film and paper base materials as the steps and chemical solutions are basically the same for each. Where major differences occur, they are noted.

Color Negative Process

The first step in the negative process is color development. Color development produces in each layer a dye image and a silver image, the amount of dye generated being proportional to the silver developed. The images are negative with respect to the exposure sources. The dye image is formed by a reaction between the developer oxidation products and a group of organic molecules called couplers to form dyes of the appropriate color in each layer. The developer solution commonly contains salts of diethylpara-phenylene diamine or its derivatives as the developing agent. The salts may be the hydrochloride or the sulfate. Certain newer developing agents, such as 4-amino-N-ethyl-N-[beta-methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate,

produce better color rendition and have reduced toxicity. In addition to the developing agent, the developer solution usually contains color-fog restrainers such as hydroxylamine hydrochloride, a solvent such as benzyl alcohol and a contrast and color balance control agent such as ethylenediamine tetraacetic acid or citrazinic acid.

The next process step stops development and removes excess developer. This can be done by washing, but usually a weak acid stop bath is used, e.g., 0.5 percent acetic acid buffered with sodium acetate to control pH, followed by a brief wash. In some cases a stop bath is used with a hardening agent.

The film or paper is then bleached to convert the developed silver image back to a silver halide in preparation for the subsequent removal of all silver from the final product by the fix solution. The color dye image remains unaffected in each layer. The bleach most commonly used in the negative process is the ferric salt of ethylenediamine tetraacetic acid (ferric EDTA). It is possible to substitute ferricyanide bleach for the ferric EDTA in some processes. This is done by some large plants incorporating centralized ferricyanide bleach systems which supply bleach to multiple processes.

After bleaching, the film or paper is fixed to remove the silver compounds and washed to remove all excess chemicals. Finally the emulsion is hardened and stabilized using a 2 percent formalin and 3 percent sodium carbonate solution, with the formalin acting as the dye stabilizer. Most color paper processes use a combination bleach-fix solution which converts silver to the halide and dissolves the halides in one operation. The typical solution contains ferric EDTA and sodium thiosulfate as major ingredients.

Color Reversal Processes

There are two different types of color reversal materials. In one, the color couplers which form the color dye image are incorporated into the emulsion layers at the time of manufacture (IC). Most color reversal materials are of this type. The second type has three black and white layers,

each sensitive to a different color. For this type of material, the color couplers are added during development (DC). The (IC) process applies to film and paper materials, and the (DC) process applies to film. The procedures and chemistry for reversal color processing are described below.

Color Reversal Process (IC)--

The first step in the color reversal process for (IC) materials is to pre-harden and develop the film or paper in a highly alkaline negative developing solution to produce a negative silver image in each layer. This developer is similar to that used for black and white reversal development. Color couplers are not affected during this step. A small amount of thiocyanate added to the developing solution aids in dissolving small, non-light sensitive silver halide grains, thus eliminating a source of image fog. Following the negative development step, the material is washed or treated in stop and hardening solutions. The emulsion is then re-exposed to a strong light source, exposing the undeveloped silver halide. The material is further developed in a color developer solution which reduces the remaining silver halide to silver and reacts with the couplers to produce a positive dye image of the appropriate color in each of the three layers. The color developer formulation is similar to the developer used for color negative materials. In some processes, a highly fogging color developer is used in place of the light re-exposure. The dye development is usually followed by hardening, stop and wash steps, which in turn are followed by bleaching. A commonly used film bleach is a potassium ferricyanide and potassium bromide solution which converts the developed silver to silver bromide. EDTA bleach is also used for certain film processes, and an EDTA based bleach-fix is commonly used for reversal papers. The film or paper is then fixed to remove the silver bromide, washed, stabilized, and dried.

Color Reversal Process (DC)--

Color reversal (DC) film processing is complicated and requires rigorous chemical control of solutions. The first development step, as with the reversal (IC) materials, forms

a negative silver image in all three layers. After this, all three layers in the emulsion are treated separately. First, the red-sensitive layer is prepared for development by exposure to red light through the base of the film. This exposes the remaining undeveloped silver halide in that layer. The other two layers, which are not sensitive to red light, are unaffected. The film is treated with a color developer that contains, among many other ingredients, a coupler which forms a red-absorbing (cyan) dye in the red-sensitive layer. As the color developing agent reduces the silver halide and forms an image, the oxidized color developer in the vicinity of the developed silver grains forms the positive cyan dye image.

After washing, the film is exposed from the top with blue light exposing the undeveloped silver halide in the top blue-sensitive layer. A yellow filter layer protects the middle green-sensitive layer. A second color developer, containing a soluble yellow coupler, produces both a silver and blue-absorbing (yellow) positive dye image in the top layer.

After a second wash, the middle layer is developed and chemically fogged in a third color developer containing a fogging agent and a magenta coupler which forms the final positive silver and green-absorbing (magenta) dye image. The film at this point has a negative silver image, a positive silver image, and a positive color dye image in each layer. Following a third wash, the silver images are removed as in the other color processes by bleaching and fixing followed by washing and drying.

PROCESSING CHEMISTRY

To make up the required solutions for processing a particular film or paper, the processor has a choice of (a) using a kit where all the necessary solution formulations are included, (b) using bulk formulations for each solution, or (c) using bulk raw chemicals. In general, small processors use kits and larger processors use bulk formulations and raw chemicals. The processor has a wide latitude in selecting formulations for the processing of black and white materials. For example, many different

developer formulations made by any one of several manufacturers can be used to develop a given black and white film. In color processing, the choice is more limited, because process solutions are formulated specifically for a particular emulsion type.

Because of the broad range of black and white processing formulations, individual processes are not identified by name; rather, formulations are named by the various manufacturers (for example, developers such as Dektol, D-76, 53-D, etc.). In color processing, where each solution formulation is more limited, the processes generally have names which define the process steps and the solution formulations. For a given color emulsion, several manufacturers may provide kits or formulations with different names, but the chemical content is quite similar.

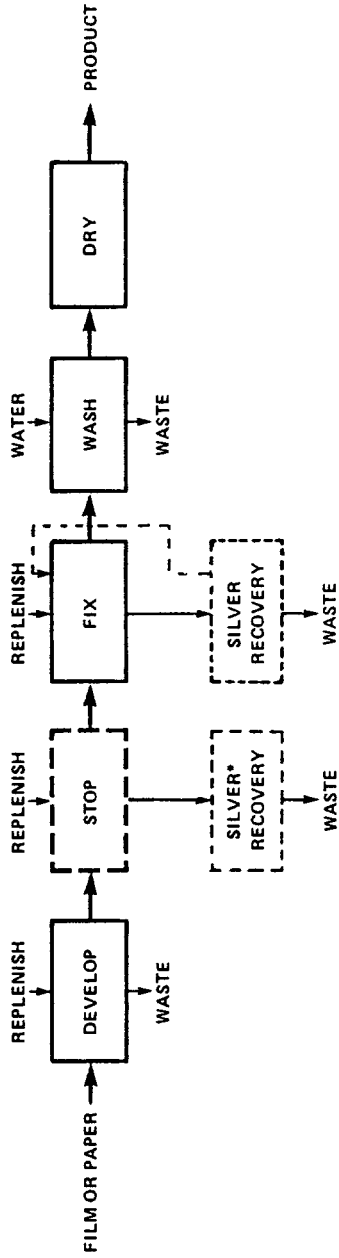
In references to black and white processing in this report, no process names are used, only the descriptors, negative or reversal. Where appropriate, color processes are referenced by name. The process name is used to identify a specific composition and sequence of processing solutions for which certain photosensitive materials are designed. Any manufacturer of photosensitive materials may produce films or papers designated for processing in any specific process. Any manufacturer of photographic chemicals may produce chemicals intended to be used for specific processing solutions in any designated process. The following is a list of the color processes most often encountered during this study.

<u>Material Type</u>	<u>Process Name</u>
Color negative process film	C-22, C-41, MC-42, ECP-1, ECP-2 ECN-1, ECN-2
Color reversal process film (IC)	E-3, E-4, ME-4, EM-25, CRI, ECO-3, E-6, E-7M, EA-5
Color reversal process film (DC)	K-12, K-14
Color negative process paper	EP-2, EP-3, MC111, 85/86
Color reversal process paper	EPR-5, EPR-100, P-10 P-18

Over the period of this study the manufacture of photographic materials designed for some of these processes has been discontinued. As the stocks of these materials are depleted there will no longer be a need for the corresponding processes. The processes included in this category are C-22, ECN-1, E-3, E-4, K-12, and EPR-5.

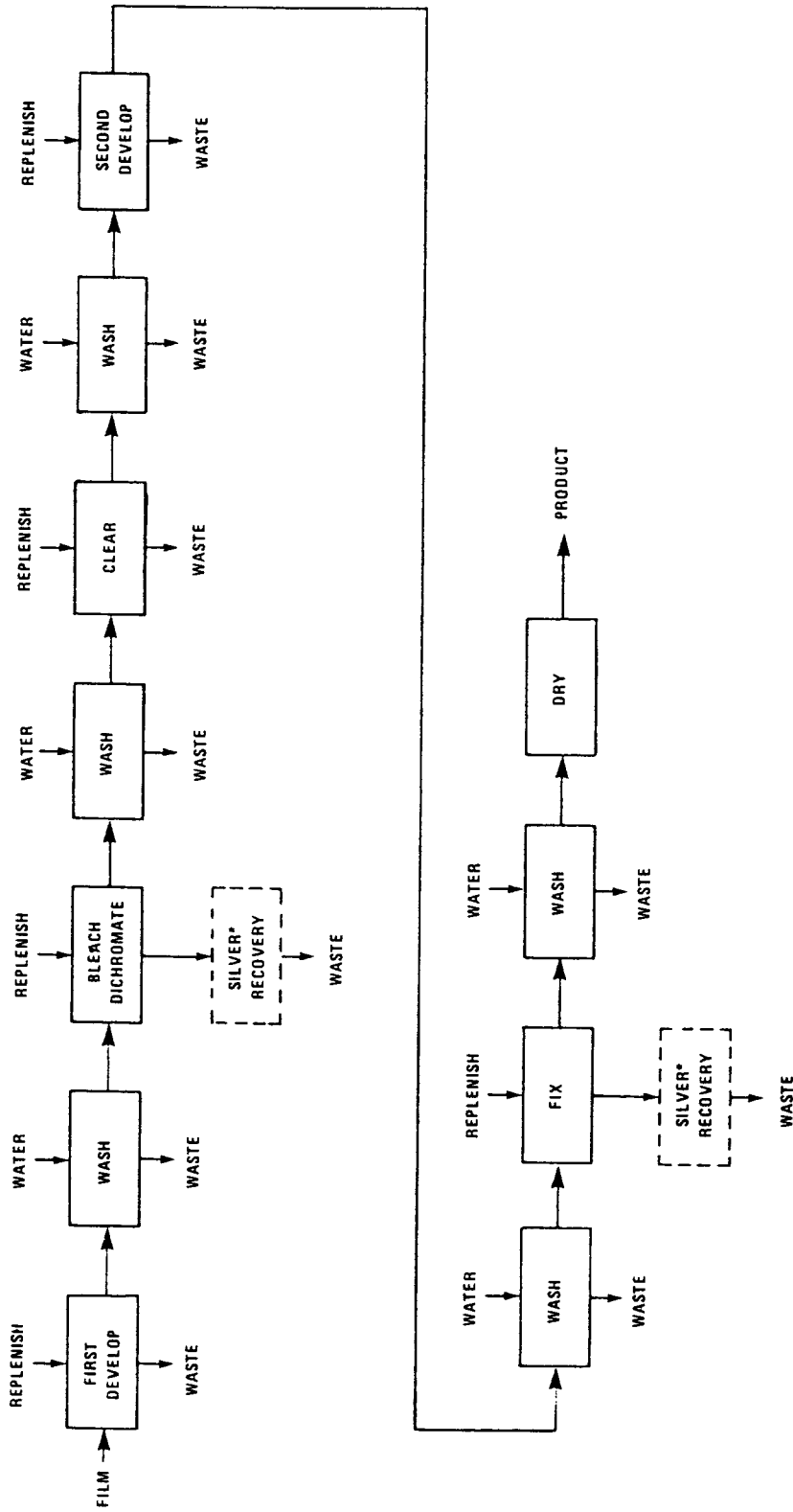
The schematic process diagrams for the listed processes are included in Figures III-1 through III-19. Dashed lines represent optional steps or operations. The optional recycle of fix is applicable only when electrolytic silver recovery methods are used. The additions of make-up chemicals, regeneration chemicals, or air required in the various bleach regeneration processes are not shown in the following schematics. This information is given in the discussion of the regeneration methods in the following subsections.

The process solution chemicals lose activity, are transformed by chemical reaction, and are contaminated by chemicals from the emulsion and by drag-in from previous solutions. There is also volume reduction or concentration changes due to absorption of solution into the emulsion and evaporation. Drag-in and drag-out of solution are usually not factors because they are approximately equivalent and cause no net volume change. To alleviate the effects of chemical transformation and volume reduction, it is common practice to replenish the solutions with fresh or



*SILVER IS RECOVERED FROM THE STOP BATH RATHER THAN THE FIX IN CONTINUOUS MACHINES THAT PROCESS BLACK AND WHITE NEGATIVE ROLL PAPER USING A DEVELOPER, STOP, AND FIX; WHEN ONLY A DEVELOPER AND FIX ARE USED, SILVER IS RECOVERED FROM THE FIX.

FIGURE III-1. PROCESS: BLACK AND WHITE NEGATIVE - FILM AND PAPER



*MAJORITY OF SILVER IS FOUND IN DICHROMATE BLEACH

FIGURE III-2. PROCESS: BLACK AND WHITE REVERSAL

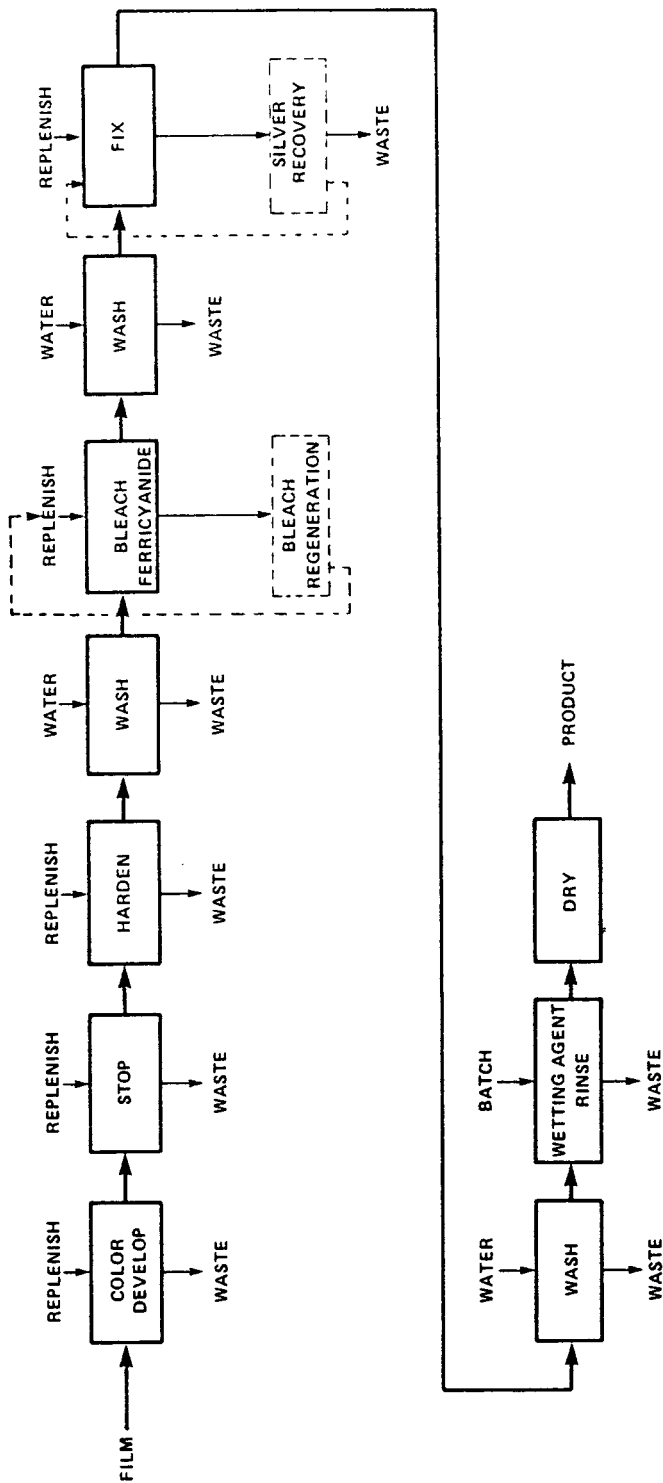


FIGURE III-3. PROCESS: COLOR NEGATIVE FILM, C-22

41

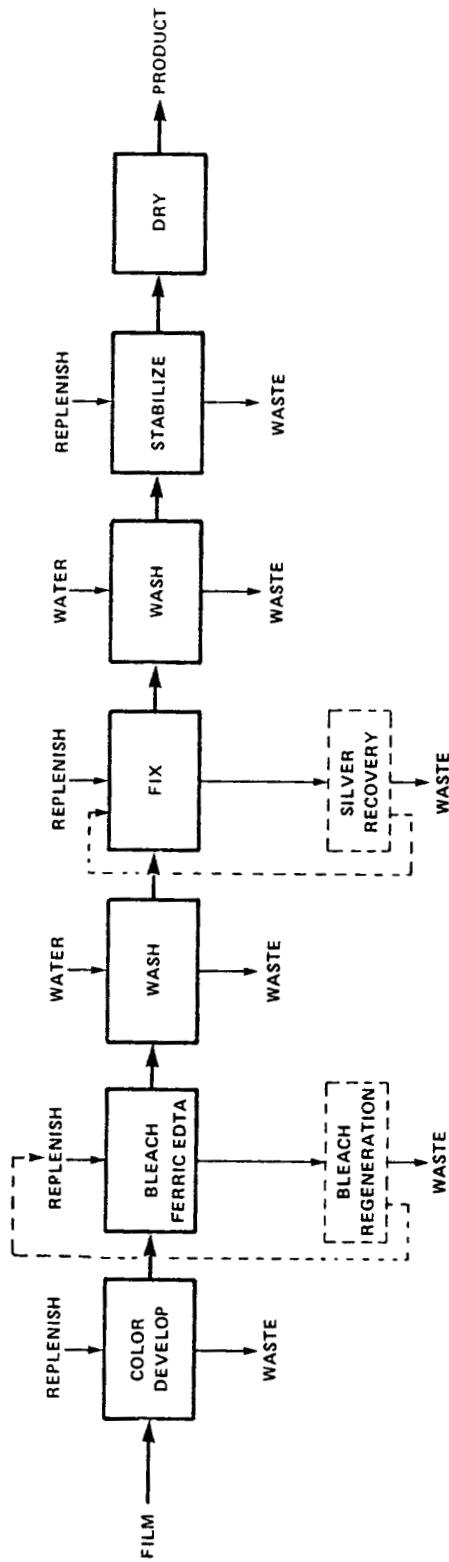


FIGURE III-4. PROCESS: COLOR NEGATIVE FILM, C-41

III-18
42

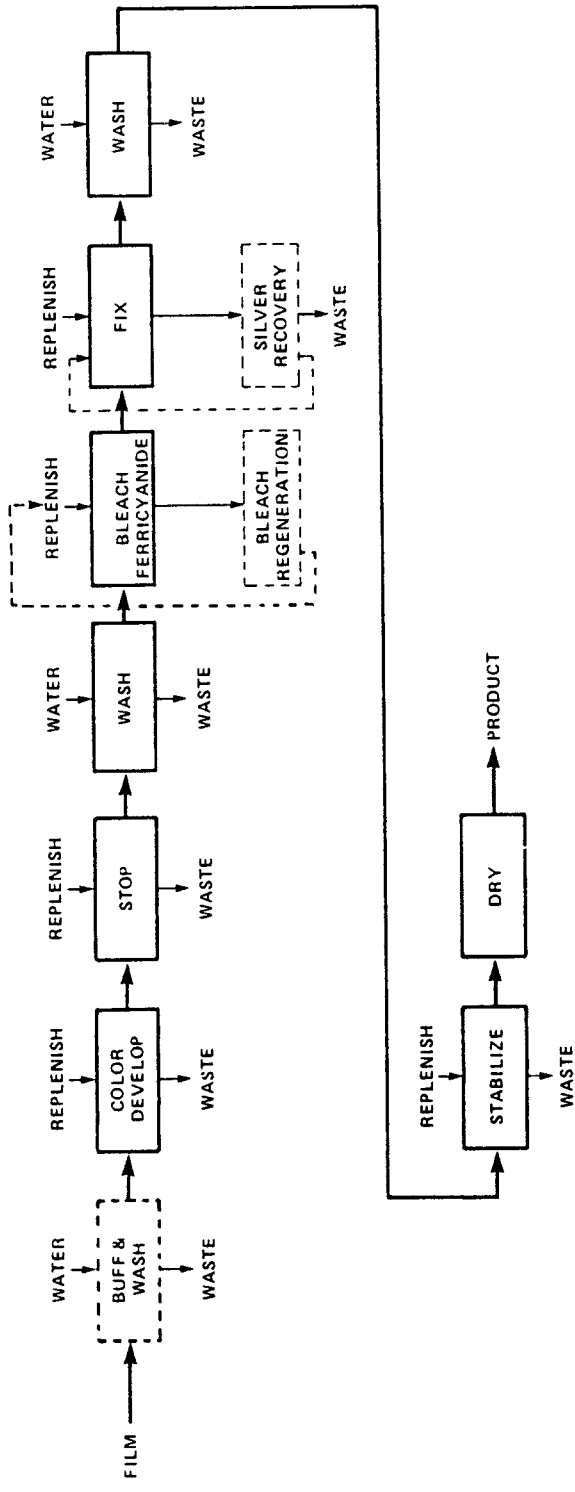
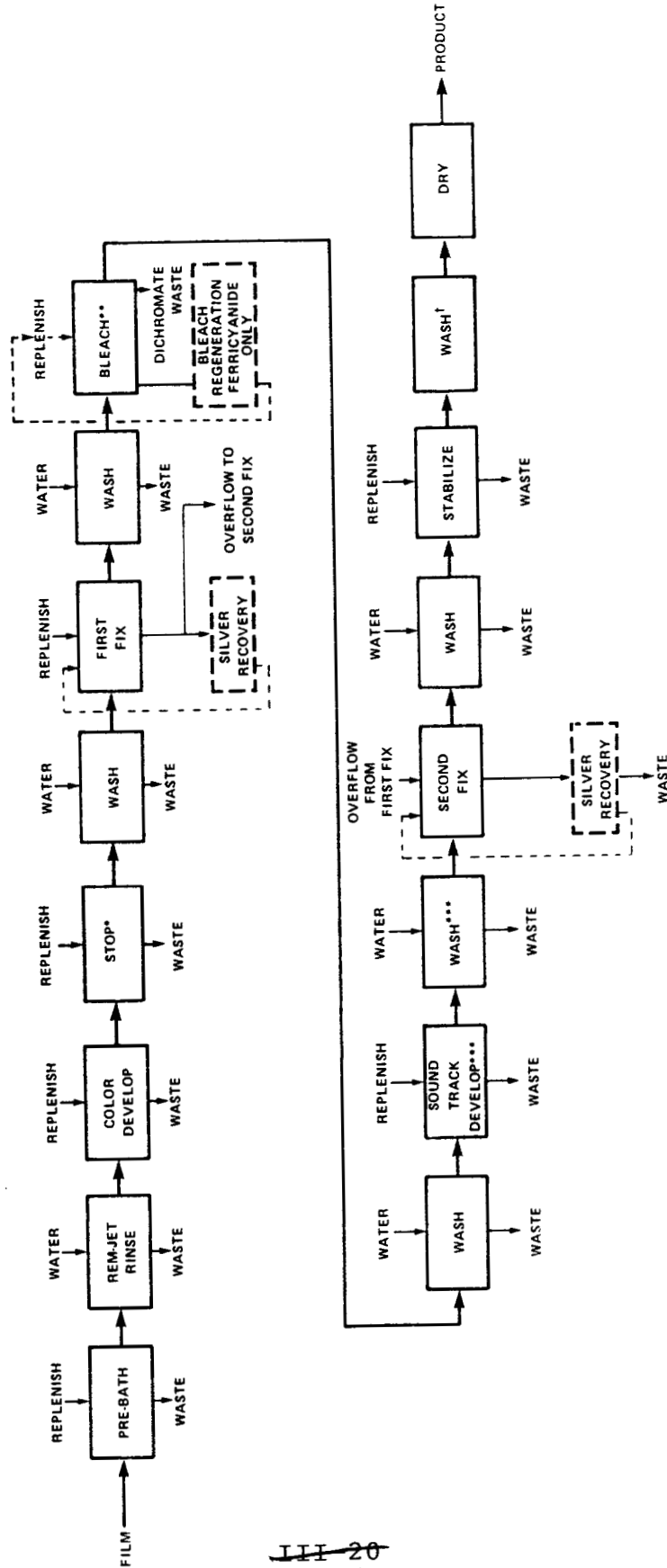


FIGURE III-5. PROCESS: COLOR NEGATIVE FILM, MC-42

III-19
43



III 20
44

* STOP USED FOR ECP 2 ONLY
 ** FERRICYANIDE BLEACH USED FOR ECP-1, ECP-2, DICHRIMATE BLEACH USED FOR ECP-1
 *** USED ONLY FOR OPTICAL SOUND TRACK PRINTING
 † USED FOR ECP-1 ONLY

FIGURE III-6. PROCESS: COLOR NEGATIVE FILM; ECP-1, ECN-1, ECP-2

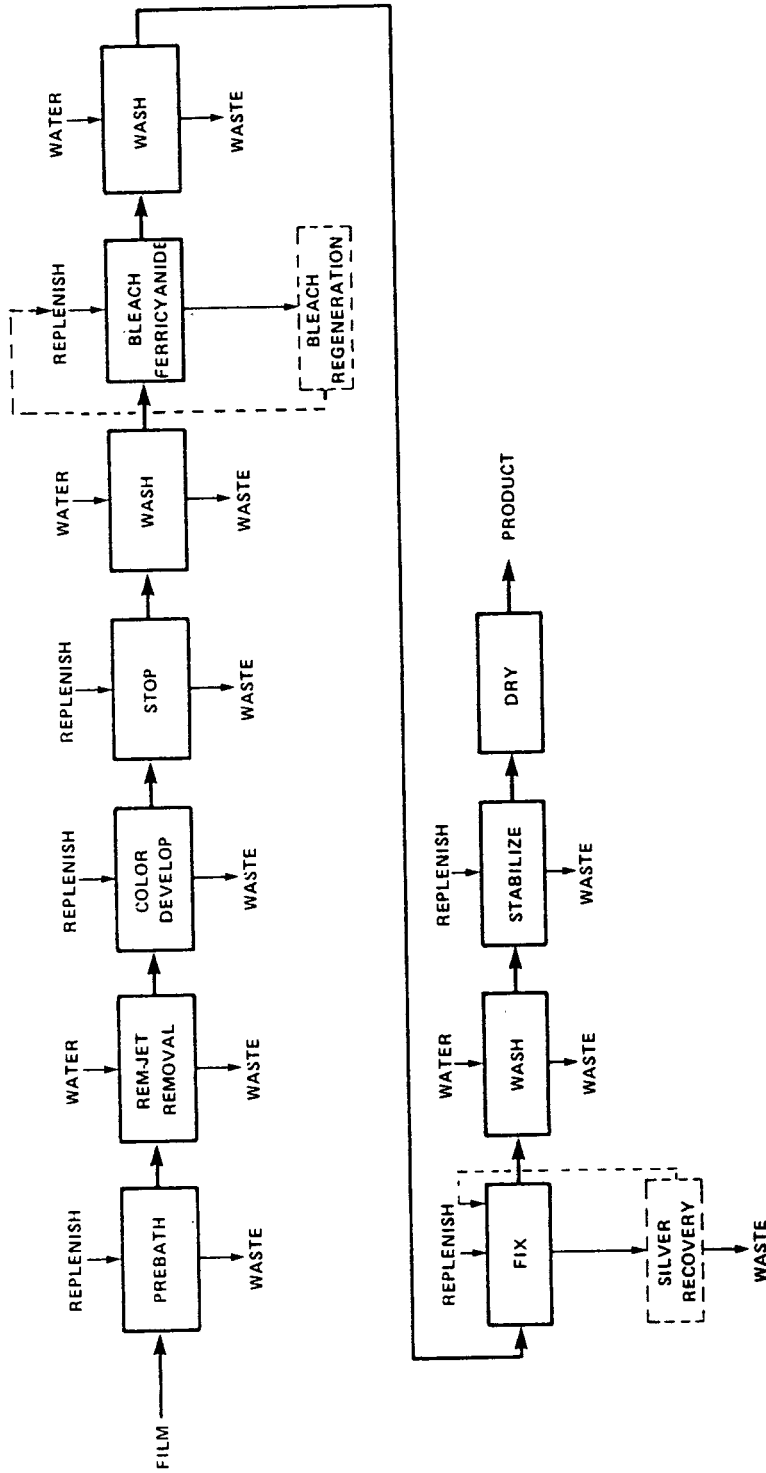


FIGURE III-7. PROCESS: COLOR NEGATIVE FILM, ECN-2

III-21
45

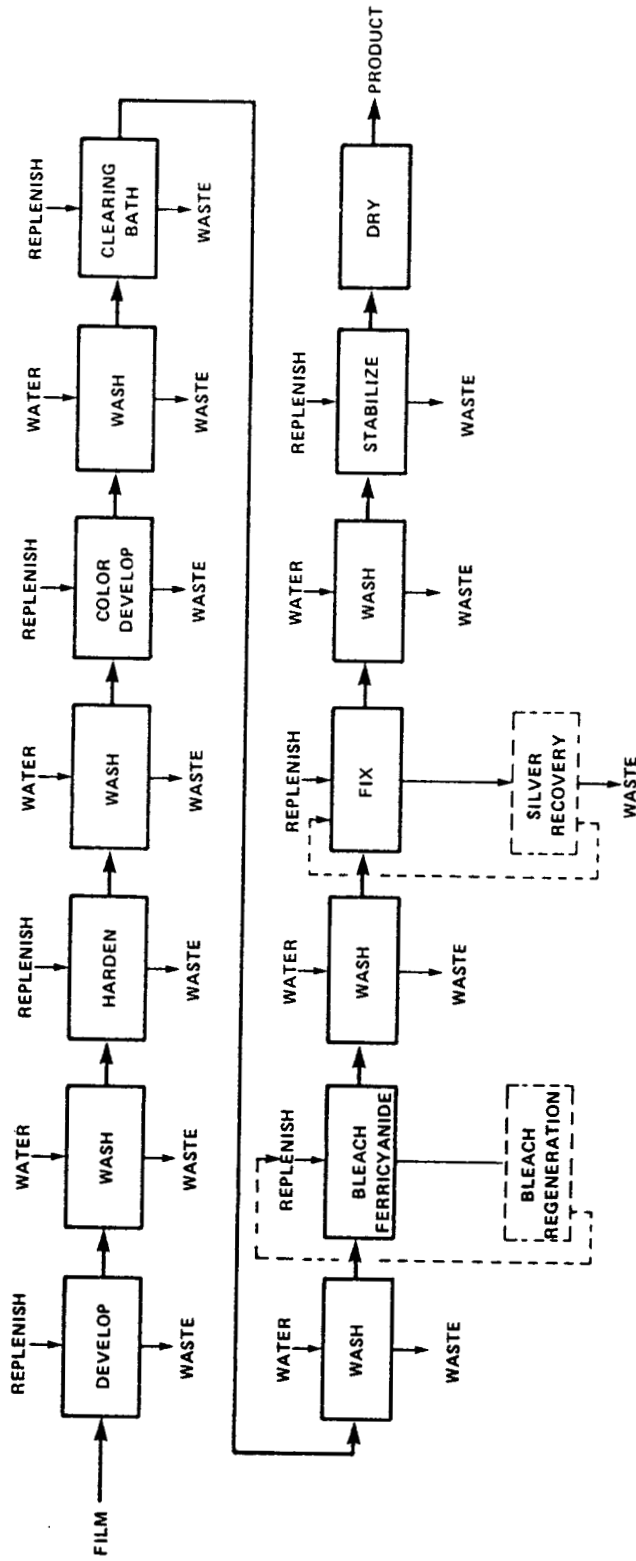
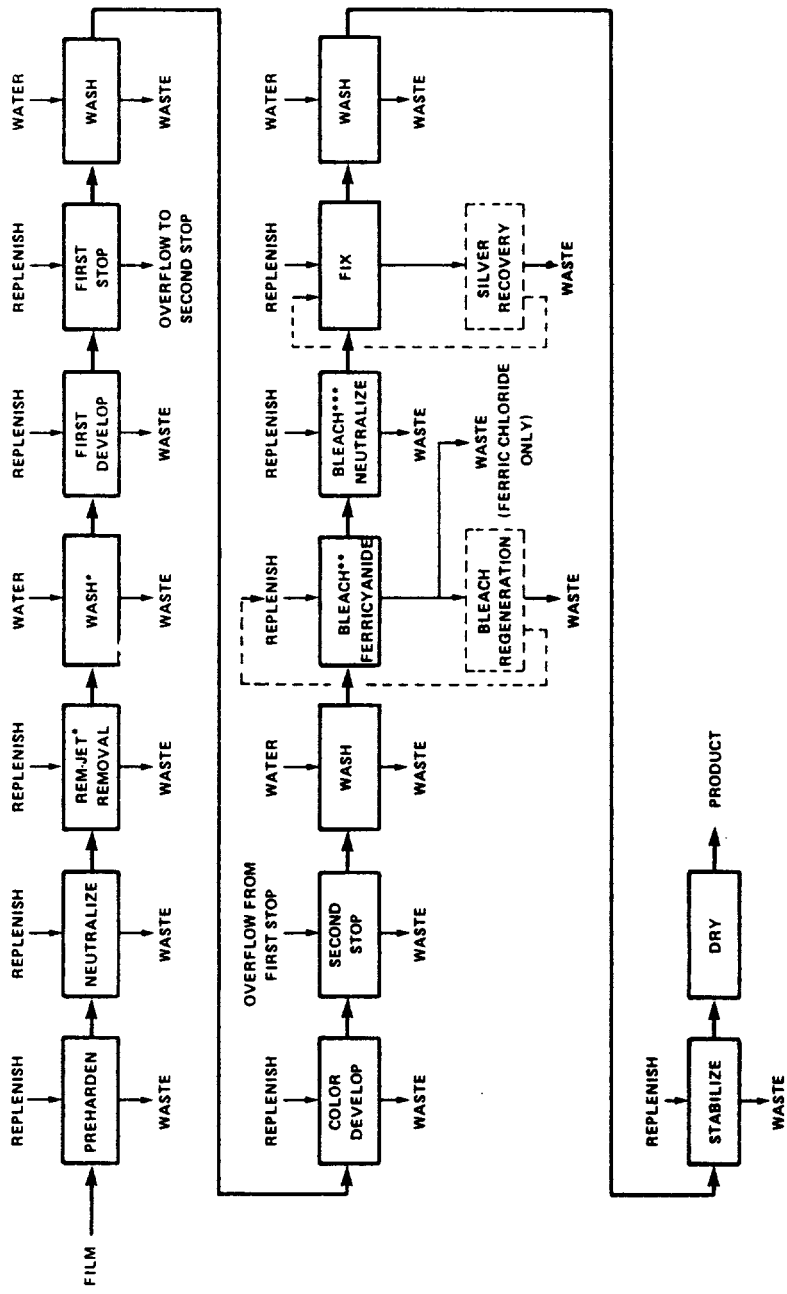


FIGURE III-8. PROCESS: COLOR REVERSAL FILM (IC), E-3

III-22
46



* NOT USED IN E-4 AND ME-4 PROCESSES
 ** EM-25 PROCESS USES FERRIC CHLORIDE BLEACH WITH NO REGENERATION
 *** BLEACH NEUTRALIZE STEP USED IN EM-25 PROCESS ONLY

FIGURE III-9. PROCESS: COLOR REVERSAL FILM (IC), EM-25, E-4, ME-4, ECO-3, CRI-1

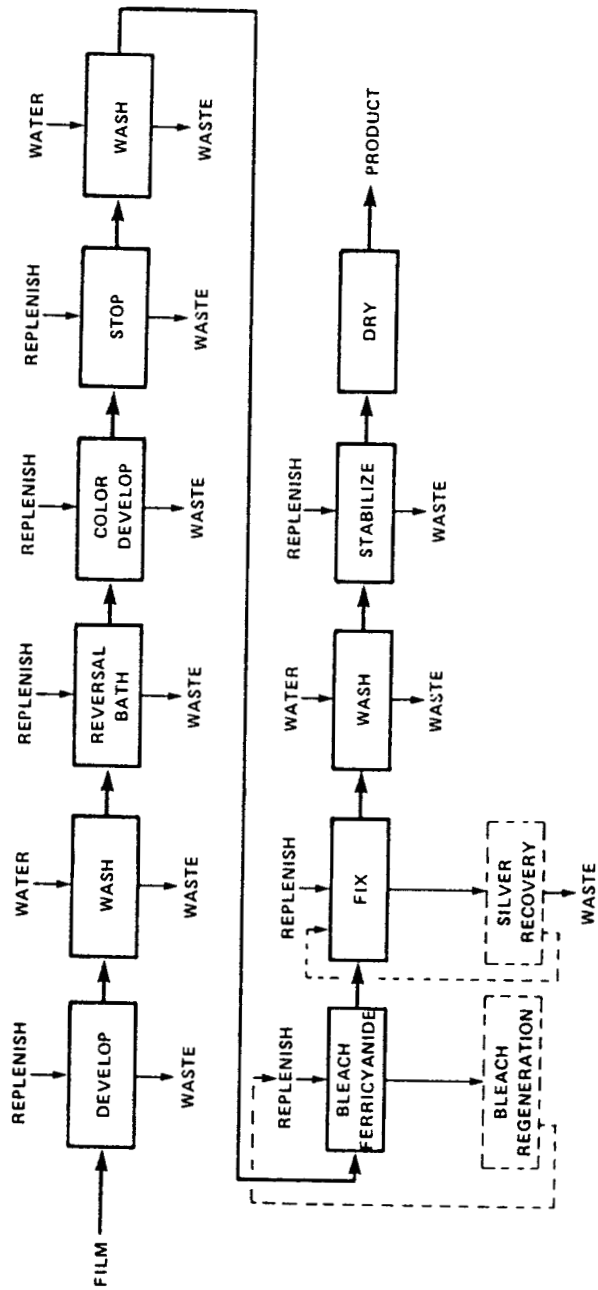
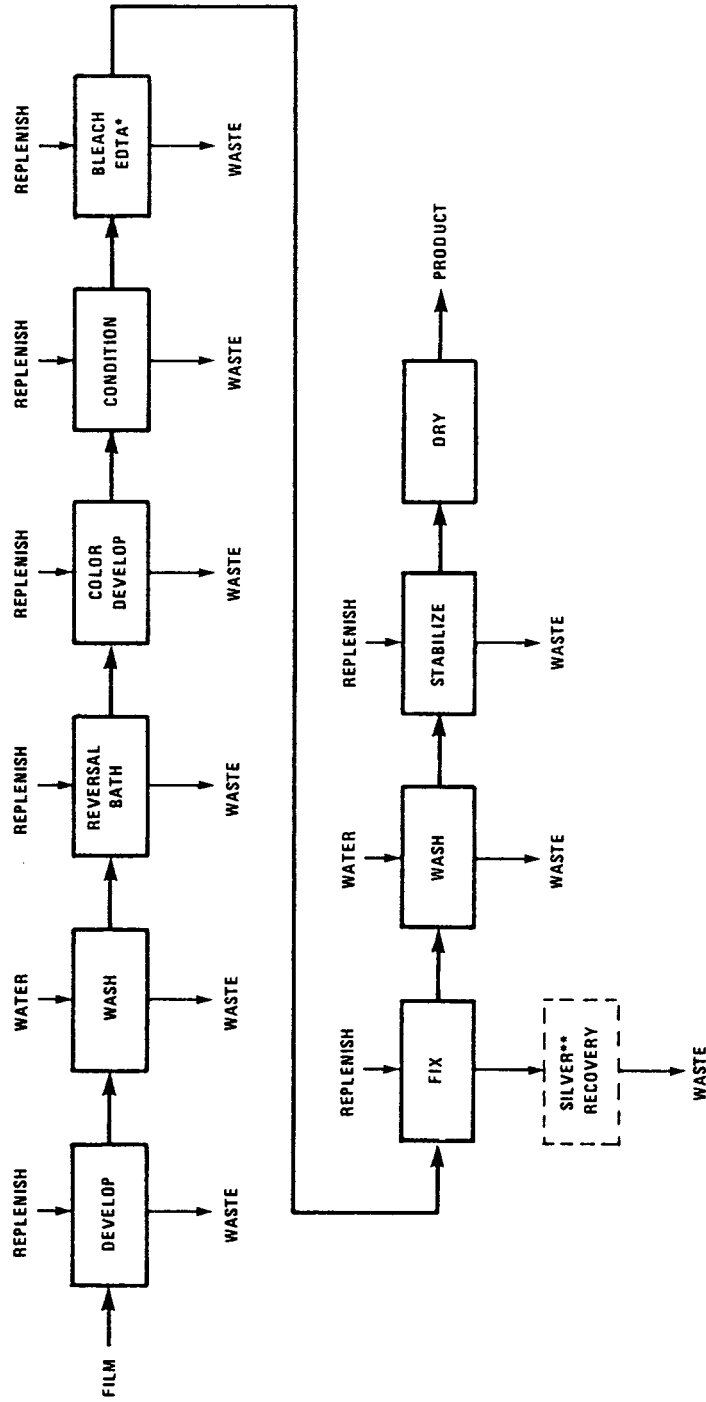


FIGURE III-10. PROCESS: COLOR REVERSAL FILM; (IC), E-7M

III-24
48



*NO REGENERATION OF BLEACH
 **NO RECYCLING OF FIXER BECAUSE OF BLEACH CONTAMINATION

FIGURE III-11. PROCESS: COLOR REVERSAL FILM; (IC), E-6

III-25
 49

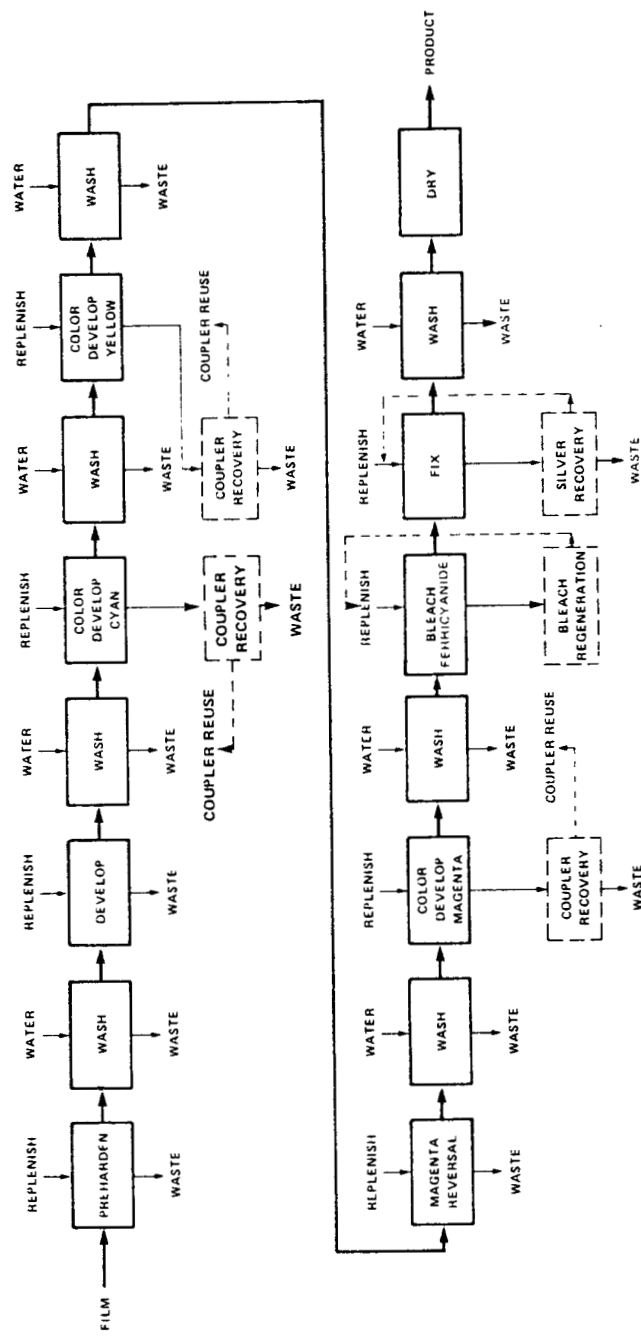


FIGURE III-12. PROCESS: COLOR REVERSAL FILM (DC), K-12

III-26
50

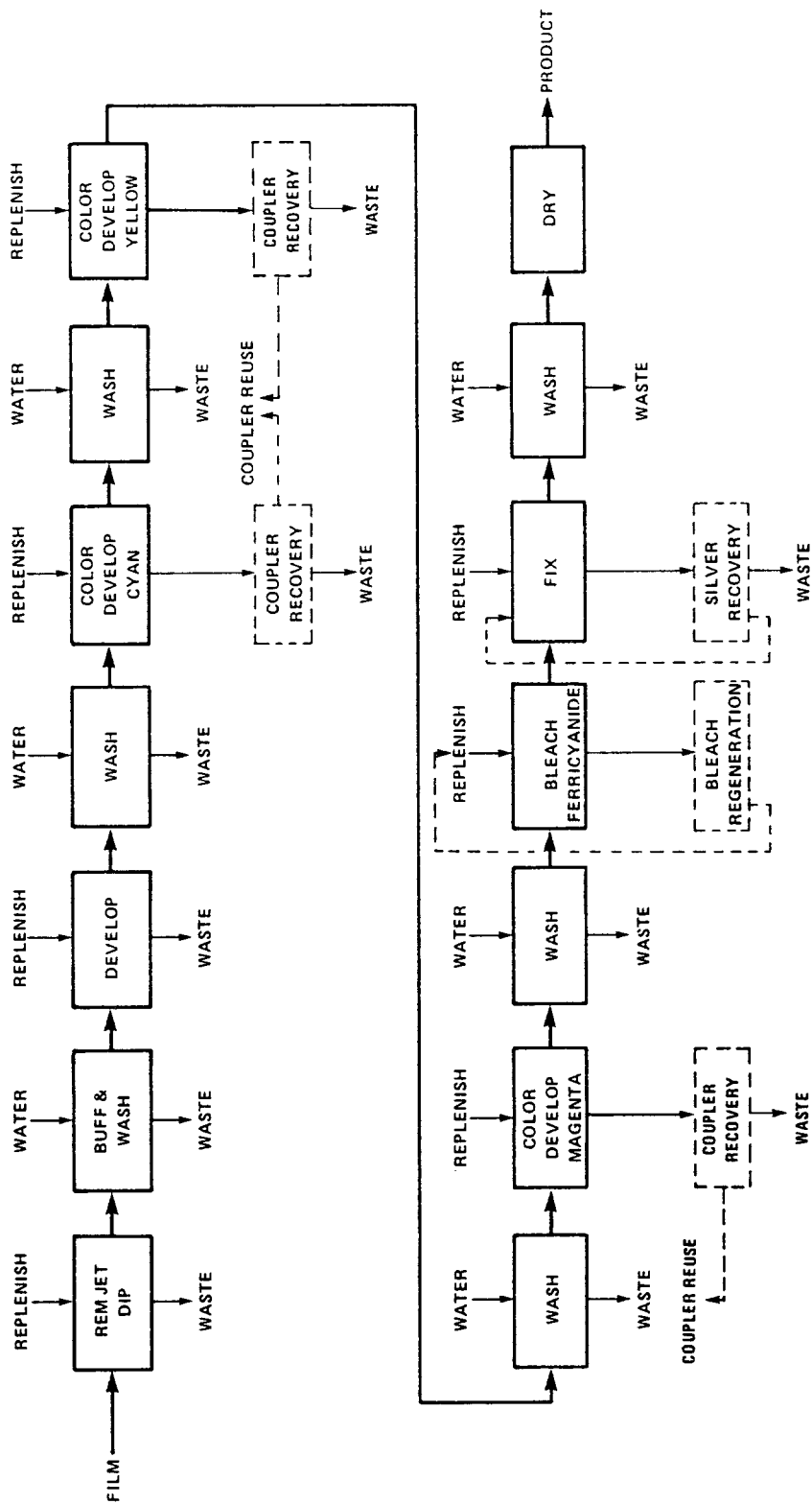
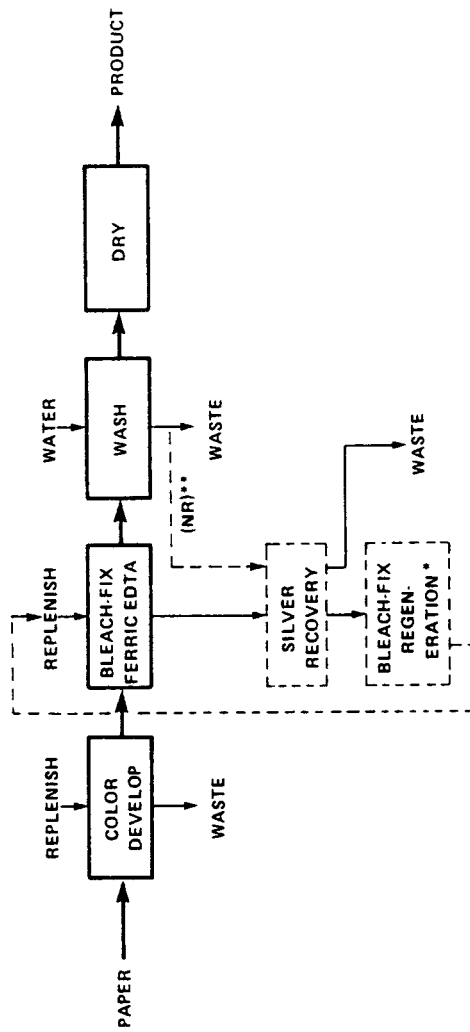


FIGURE III-13. PROCESS: COLOR REVERSAL FILM (DC), K-14

III-27
15



*NO REGENERATION WITH NR BLEACH FIX
 **SILVER RECOVERY FROM WASH USED IN EP-2 PROCESS WITH NR BLEACH FIX

FIGURE III-14. PROCESS: COLOR NEGATIVE PAPER, EP-2

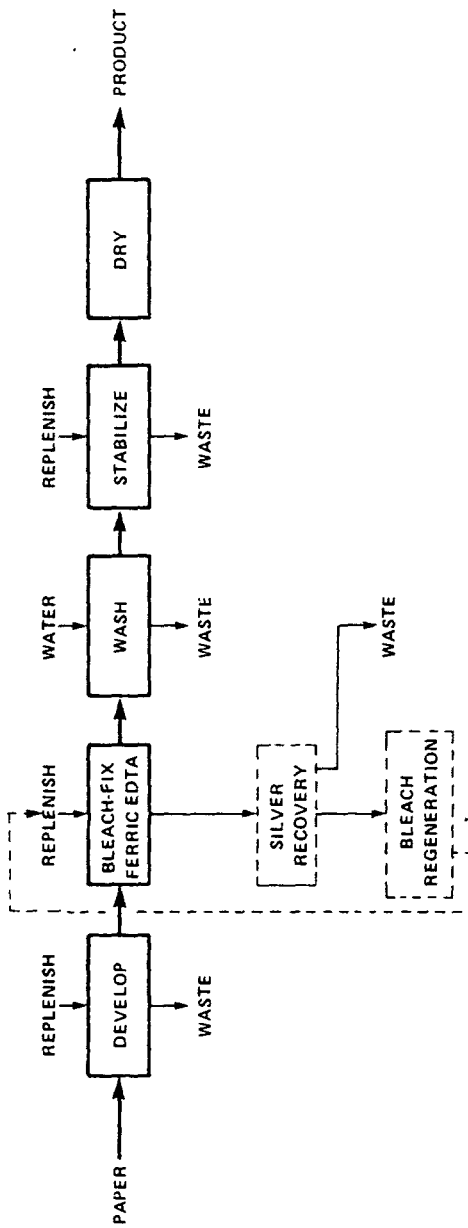


FIGURE III-15. PROCESS: COLOR NEGATIVE PAPER: EP-3, 85/86

III-29
53

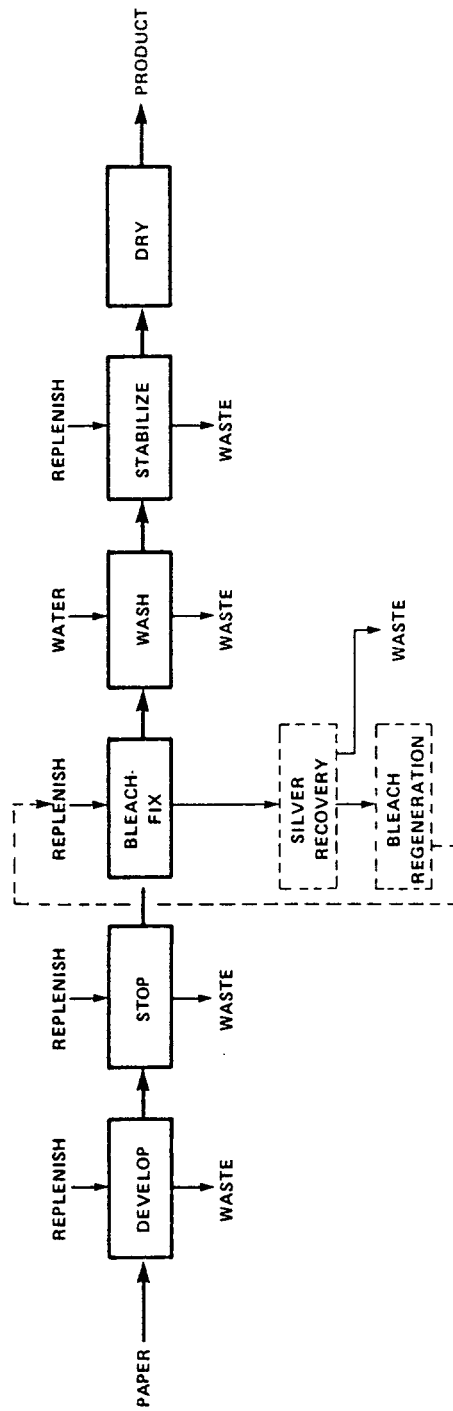


FIGURE III-16. PROCESS: COLOR NEGATIVE PAPER, MC 111

III-30
54

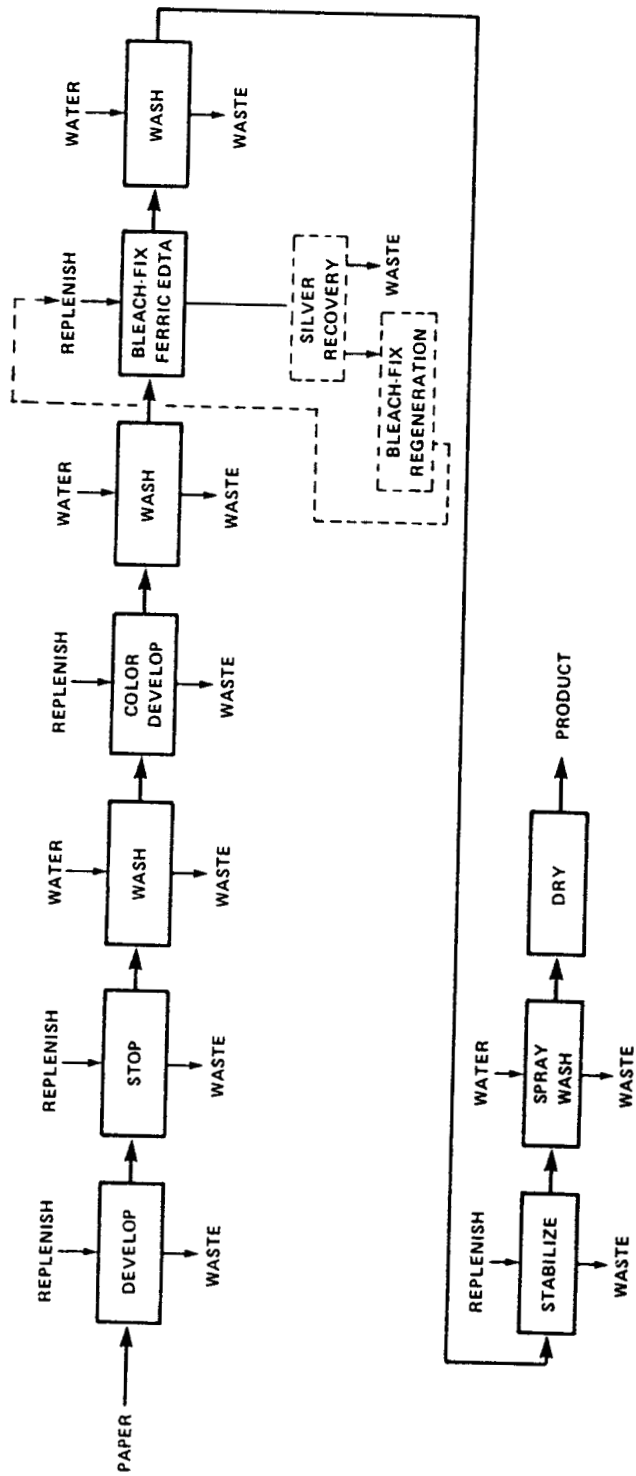


FIGURE III-17. PROCESS: COLOR REVERSAL PAPER, EPR-5, EPR-100

III-31
55

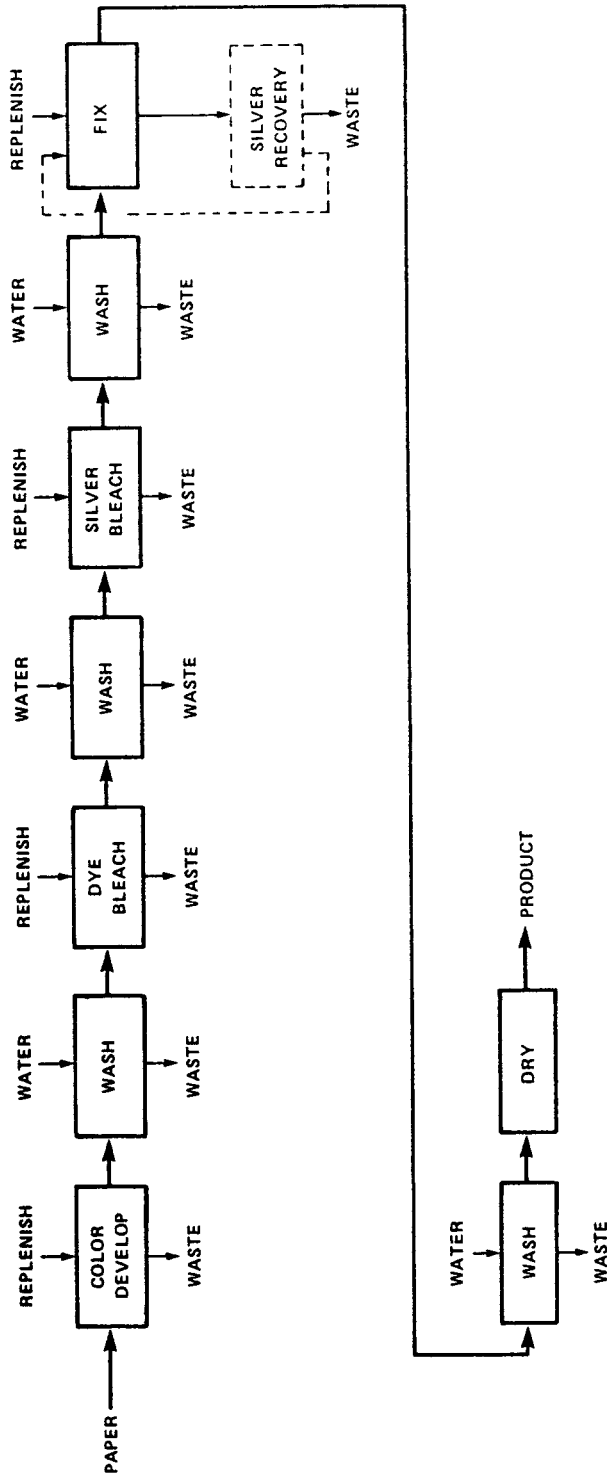


FIGURE III-18. PROCESS: COLOR REVERSAL PAPER, P-10

III-32
56

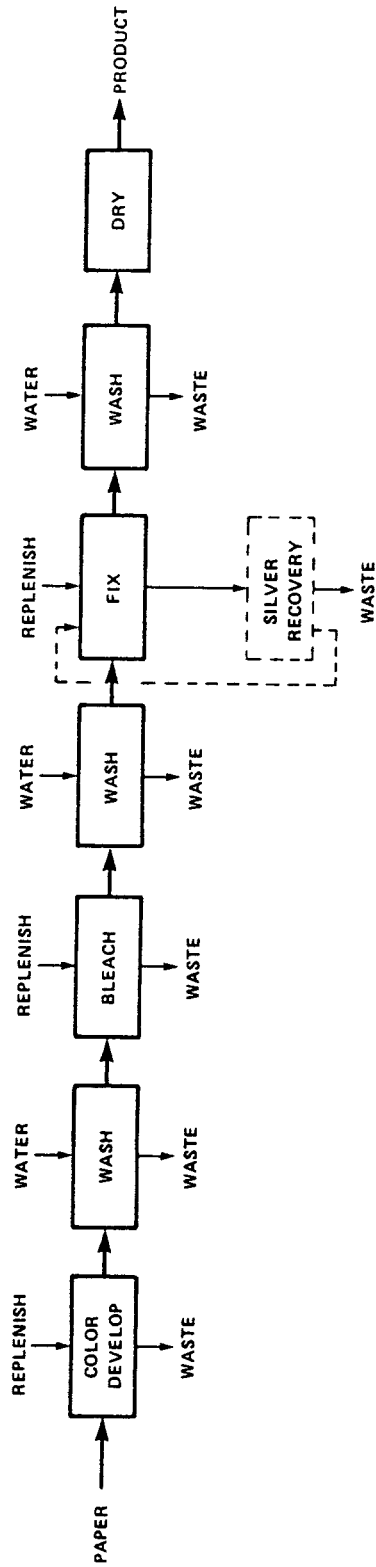


FIGURE III-19. PROCESS: COLOR REVERSAL PAPER, P-18

reconstituted chemicals. For example, with use, a developer gradually loses its effectiveness. The concentration of the developing agent and the pH decrease, and the halide ion accumulates. The developer replenishing solution usually contains a higher concentration of developing agents than the original solution and little or no bromide. It also contains alkali to help maintain a constant pH.

The replenishment is at a continuous or programmed rate on continuous process machines. The rate of replenishment is greater than the normal volume reduction resulting in an overflow of solution. This reduces accumulation of unwanted chemicals in the process tank. Batch replenishment may be used on "dip and dunk machines" or with manual processing.

Some processors practice a type of replenishment called "replenishment on demand" whereby the critical constituents (for example, chromate) of the solution are monitored and replenishment is done by batch in the required amount when these constituents are reduced to predetermined levels. Although overflow is still allowed to occur to reduce unwanted chemical accumulation, proponents of this method claim that the waste load is reduced from that found in continuous replenishment because of higher efficiency. A further explanation of this method is given in a subsequent section of this report, Reconstitution of Dichromate Bleach.

PROCESSING EQUIPMENT

Photographic materials may be processed either manually or in automatic processing machines. Manual processing and certain automatic "drum" machines are suited to custom processing or processing small quantities of material. Manual processing is predominately suited to very small labs but may be found in the larger labs as well. Automatic processing machines (with the exception of drum processors) have the capability for high production rates and are suited to the larger labs.

A manual processing method, sometimes called "sink line" processing, consists of manually placing, for the correct time and in proper sequence, exposed photo material in each of a series of trays or tanks containing the required

chemical solutions. A second manual technique utilizes a single tank or drum. The photo material is placed in the tank or drum and the first processing chemical solution is poured into the container. After remaining for the proscribed time, the solution is dumped and replaced with the second solution. This process is continued until all solutions have been used. An automated version of this process, called automatic drum processing, consists of a motorized rotating drum and preprogrammed, electrically operated solution fill and dump valves.

Most photoprocessors, as included in this study, handle large quantities of film and paper with automatic processing machines. The three types most widely used are "dip and dunk," roller transport, and continuous length processors.

The "dip and dunk" processor, an automated version of "sink line" processing, is generally used for roll films. The machine consists of a series of deep tanks, elevator or lifter mechanisms, and a movable track or chain drive. The film is attached to hangers, automatically transferred from tank to tank by the lifter mechanism and deposited in the tank by the movable track. A limited adjustment of the processing times in individual tanks is possible. The film is dried in a drying tunnel that is part of the machine. A second type of dip and dunk processor is an automatic version of manual basket processing. The film, plates or paper are loaded onto reels or baskets. The entire assembly is moved on an overhead gantry that raises and lowers the basket into each process tank at preprogrammed times.

Roller transport machines consist of a series of solution tanks and use a combination of pinch rollers and belts to feed the photo materials through each solution tank in succession. Roller transport machines are commonly used for sheet film, narrow widths of professional and aerial film and large format (up to 1.3 meters wide) prints. They require no leader and are suited to the processing of single pieces of film or paper at high production rates.

The continuous length processor is generally used for movie films and long rolls of film and paper. Short rolls can also be accommodated by splicing the short rolls together

end on end to make a long length. The continuous length processor consists of a series of deep tanks, roller racks or transports in each tank, and feed and take-up mechanisms. The feed and take-up mechanisms usually include a slack box to facilitate splicing without stopping the main drive. The film travels back and forth in each processing tank over a series of rollers on the rack. The path length and linear film speed are adjusted to give the desired residence time in each tank. Upon exiting a tank, the film travels to the next tank over roller connections between racks. Continuous processing units are time-consuming to thread and are commonly threaded with leader stock. The starting end of a material to be processed is attached to the leader end which then guides the material through the machine. New leader is attached to the end of the processed material and remains in the machine ready for the next run. It is common to run leader before and after production runs for quality control purposes to inspect for mechanical abrasion problems and chemical balance. A short photosensitive test strip is attached to the leader for the chemical balance check. During leader run there is generally either no replenishment or reduced rate replenishment of some solutions. Wash water usually runs at the normal production rates. The wastewater hydraulic load is comparable to production loads. Pollutant loading is reduced to essentially that caused by solution carryover into the wash waters. No additional silver loading occurs since the leader has no silver emulsion.

The ratio of leader to production varies widely and depends on the machine type and the materials processed. "Dip and dunk" machines require no leader. Roller transport machines have pinch roller feed guides which require no leader. Plants that predominately use these machines have a very low leader to production material ratio. On the other hand, plants using continuous machines and processing amateur materials consisting of short lengths of narrow film and paper may have a leader to production material ratio of one or more, i.e., they may run more leader than production material. If possible, the processor will splice the short film end on end to create a long continuous length and reduce the need for leader. However, this is often not possible because of the promise to the customer to return the finished product quickly. A quick turnaround time

requires machines to be continually "at ready," resulting in numerous short runs, relatively large amounts of leader run and frequent quality control checks. The movie labs, which use similar machines and process similar film widths, have leader to film ratios on the order of 0.1 to 0.5 because they process comparatively long lengths and can plan their production more efficiently.

Most automatic processing machines have automatic agitation and solution replenishment. The method most commonly used for agitation is called gas-burst agitation which consists of releasing gas through tiny holes in a distributor plate in the bottom of the solution tank at controlled intervals. The gas bubbles formed during release provide the random agitation pattern necessary for uniform results. Oil-free compressed air is usually used except in the developers where nitrogen is used to prevent oxidation of developing agents.

IN-PROCESS CONTROL TECHNOLOGIES

In-process controls are used in the photographic processing industry primarily for the conservation or recovery of raw materials for economic purposes and secondarily for pollution abatement purposes. Controls include: (1) the recovery of raw materials such as silver and organic couplers, (2) the regeneration of processing solutions for recycle such as fix and bleach, and (3) various housekeeping practices such as water saver controls and squeegees.

Effect of In-Process Controls on Product Quality

In the consideration of in-process controls, which involve the reuse of solutions, recycle of wash water, or other modifications of standardized procedures, two major precautions should be taken to ensure that (1) the control is properly applied and (2) once applied, the control is properly maintained. Any of these controls, if not properly applied and maintained, can cause immediate or long-term, adverse effects on product quality. For example, dirt build-up can immediately cause pinholes, spots, and scratches; trace chemical build-up, improper chemical balance in the solution, and insufficient chemical removal

from the emulsion can cause (1) stains and improper color balance in the short term and (2) poor dye stability and stains in the long term.

The first precaution concerns proper application of the in-process control on a process specific basis, i.e., successful application on one particular process does not guarantee success on another. When a control is applied to a particular process, it should be established, by testing product quality, that there are no short- or long-term adverse effects. The short-term tests include inspection for stains, spots, and scratches; color balance checks against standards; and hypo retention tests. Long-term effects are somewhat more difficult to evaluate. Current techniques involve subjecting processed test material to accelerated aging conditions prior to performing quality tests.

The use of many of the various in-process controls, which are discussed in detail in the following subsections, has been demonstrated and accepted. Ferricyanide and EDTA bleach regeneration have been established on most color processes, and fix recycling has been successfully used on many processes. On a more limited basis, countercurrent washing and wash water recycle have been established for some processes. Developer recycle has been successfully used on a few color paper processes. Low flow prewash is still being evaluated.

The second precaution concerns proper use and maintenance of the in-process control to ensure continued high standards of product quality. In some cases, strict adherence to recommended maintenance and use procedures may be sufficient to ensure a quality product. In others, careful chemical monitoring of process solutions or wash water and periodic product tests may be required in addition to in-process control equipment maintenance and use requirements. (Note that in-process control use procedures may require chemical monitoring of some solutions.) Finally, the origin or end-use of the material being processed may have some bearing on the use of a particular in-process control. Solution regeneration and wash water recycle do increase the risk of reduced long-term stability or product damage. In

cases where a process is used for unique film originals or where the product must have archival storage capability, the risks imposed by use of an in-process control may be unacceptable.

Silver Recovery

Two photoprocessing waste solutions contain essentially all silver removed during processing: (1) the fix or bleach-fix overflow and (2) the post-fix wash water.

The state-of-the-art of silver recovery from the fix and bleach-fix processing solutions includes metallic replacement, electrolytic recovery, and chemical precipitation. Ion exchange and reverse osmosis are other methods that can be used alone or in combination with conventional silver recovery systems. However, these are generally considered suitable only for dilute solutions of silver, such as the polish desilvering of effluent from a silver recovery unit or wash water desilvering.

These silver recovery systems can be used in a variety of ways. It is typical to have a primary silver recovery unit, which removes the bulk of silver, in combination with a "tailings" unit. Tailings consist of the relatively low silver concentration effluent from a primary silver recovery system. A tailing unit is used as a secondary or polishing unit for additional silver recovery. The typical system consists of an electrolytic primary unit and a metallic replacement tailing unit. A silver recovery system can be devoted to a single process line or be used to remove silver from the fix from several or all process lines in a plant. The multiple use systems are found in the larger plants. Sometimes a separate fix system is used for processing unique original film to reduce the possibility of inter-process contamination (when desilvered fix is recycled to the process) and the resultant damage to irreplaceable originals.

Metallic Replacement

Metallic replacement occurs when a metal, such as iron, comes in contact with a solution containing dissolved ions

of a less active metal, such as silver. The dissolved silver, which is present in the form of a thiosulfate complex, reacts with solid metal (iron); the more active metal goes into solution as an ion, and an ion of the less active metal becomes solid metal (silver).

Silver ions will displace ions of many of the common metals from their solid state. Because of its economy and convenience, iron in the form of steel wool is used most often. Zinc, as a replacement metal, can also be effective, but it is not used because of its relatively higher toxicity and greater cost. Aluminum has also been used as a replacement metal but is not commonly used because the simultaneous generation of hydrogen gas could be hazardous.

For most efficient operation, the pH of the solution passing through the metallic replacement unit should be between 4 and 6.5, with an optimum between 5 and 5.5. Below a pH of 4, the dissolution of the steel wool is too rapid. Above a pH of 6.5, the replacement reaction may be so slow that an excessive amount of silver would be lost because of the long reaction time required.

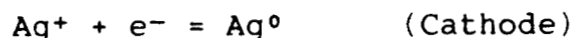
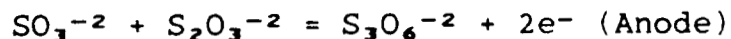
Silver recovery by metallic replacement is most often carried out using commercially available units consisting of a steel wool filled plastic bucket with appropriate plumbing. Typical practice is to feed waste fix to two or more canisters in series or series-parallel combinations. For two canisters in series, the first canister removes the bulk of the silver and the second unit polishes the effluent of the first and acts as a safety factor if the first unit is overused. When the first unit is exhausted, it is common to replace it with the second and put a new unit in the place of the second. Silver concentrations in the effluent from a single unit average 40 to 100 mg/l over the life of the unit versus a range of 0.1 to 50 mg/l when two canisters are used in series.

Desilvered fix is not recycled because of the iron contamination. The average iron concentration in the cartridge effluent, over the life of the cartridge, is 4,000 mg/l. However, this is not a problem with bleach-fix which contains iron complexed with EDTA as an active ingredient.

Because of this, metallic replacement silver recovery is a commonly used first step in the regeneration of bleach-fix.

Electrolytic Recovery

This silver recovery method requires the application of direct current across two electrodes in a silver-bearing solution causing metallic silver to deposit on the cathode. Sulfite and thiosulfate are oxidized at the anode as follows:



Approximately 1 gram of sodium sulfite is oxidized for each gram of silver plated. Considerable agitation and large plating surface areas are necessary to achieve good plating efficiency and high quality silver up to 96-98 percent pure. Lower silver purity levels are usually achieved in tailing cells. The cathodes are removed periodically, and the silver is stripped off. Care must be taken to prevent the current density in the cell from becoming too high to prevent "sulfiding." Sulfiding is the result of decomposition of thiosulfate at the cathode. The sulfide contaminates the deposited silver and reduces recovery efficiency. The higher the silver concentration the higher the current density can be without danger of sulfiding. As the silver is plated out of solution, the current density must be reduced.

Electrolytic units can be used for primary or tailing silver recovery. Primary electrolytic systems are typically installed in two basic ways. One is a batch recovery system where overflow fix from a process line or lines is collected in a tank. When sufficient volume is reached, the waste fix is pumped to an electrolytic cell for the silver removal process. The desilvered fix is either discharged or reused. For reuse, it is pumped to a mix tank where chemicals are added to bring it to replenishment strength. Primary batch system cells are usually designed to desilver the fix at

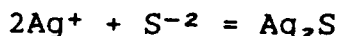
fairly high starting silver concentrations of about 5,000 mg/l. The silver concentration in the effluent is typically about 200-500 mg/l but can be reduced to 20-50 mg/l with additional treatment time and careful control of current density. An electrolytic tailing cell typically achieves the lower range because the process can be optimized for low starting silver concentrations.

The second primary electrolytic recovery method is to remove silver from the fix solution from one or more process machines in a continuously recirculating system at approximately the rate at which silver is being added by processing. The recovery cell is included "in-line" as part of the recirculation system. This continuous removal technique has the particular advantage of maintaining a relatively low silver concentration in the fix processing solution so that the amount of silver carried out with the processed material into the wash tank is minimized. The silver concentration in the fix can be maintained in the range of 500 to 1,000 mg/l, the lower limit being primarily a function of residence time in the cell, i.e., system flow rate.

The recycling of desilvered fix solution, whether by an "in-line" continuous system or by batch, requires adequate monitoring and process quality control to protect product quality. Parameters which should be monitored to maintain the physical and chemical properties of the fix solution include pH, silver, and sulfite concentrations.

Chemical Precipitation

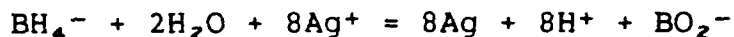
Chemical precipitation is a relatively uncommon method for recovery of silver from photographic processing waste solutions but is practiced widely in the photographic supplies manufacturing point source category. Silver may be precipitated from fixers with sodium sulfide:



The precipitation is quantitative in an alkaline solution, and the resultant silver sulfide has a solubility product of 10^{-50} making it one of the most insoluble substances known.

The physical characteristics are not as favorable as the chemical characteristics. Precipitation must be carried out in alkaline media to avoid the generation of hydrogen sulfide. Silver sulfide tends to form colloidal suspensions. Its very small particle size makes filtration difficult and the filter cake produced is extremely dense. Diatomaceous earth filter aid can be used to improve filtration. About three grams of filter aid are required for each gram of silver, if a conventional filter press is used.

Sodium borohydride is also an effective precipitant for silver:



This precipitating agent can also be used to treat photographic processing wash waters. Sodium sulfide requires very little excess, while borohydride requires significantly more than the stoichiometric reaction quantity to complete the reaction. A major difference between the two precipitating agents is the resulting silver quality. Sodium borohydride produces elemental silver of 90 to 95 percent purity. The sulfide addition generates silver sulfide containing 87 percent silver. Silver concentrations as low as 0.1 mg/l can be achieved by either method.

In a typical system, the precipitating agent is mixed with the silver-bearing waste solution in a batch reaction tank equipped with automatic pH control. The pH is maintained above 7 to avoid releasing toxic hydrogen sulfide gas when sodium sulfide is used.

The optimum pH range for sodium borohydride precipitation is 6.5 to 6.8. The solid particles formed (1-2 microns) are allowed to settle before filtering.

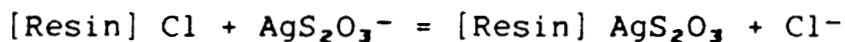
Solutions treated by sodium sulfide or sodium borohydride cannot be reused in the photographic process.

Silver Recovery from Wash Waters

Even with an efficient fix solution silver recovery system and squeegee use at the exit of the fix tank, up to 10 percent of the available silver is lost to the after-fix wash water by carryover. The silver concentration in the wash water is typically in the range of 1 to 50 mg/l and it has not been found practical to use the previously described conventional silver recovery methods for recovery of this silver. Thus, the concentration of silver is generally too low for effective use of electrolytic or metallic replacement recovery methods. In addition, the iron by-product from metallic replacement precludes the possible wash water reuse without extensive treatment. Although precipitation is technically satisfactory, it is too slow and too expensive because of raw material and filtration costs to be economical.

Two methods have been found to be effective and are currently in use for recovery of silver from wash water, namely resin ion exchange and reverse osmosis (RO). A third method called "low flow prewash" has been used on an experimental basis at two plants. This consists of apportioning the after-fix wash water into two segments, a low volume, high silver concentration prewash and a final wash of low silver content. Silver can be removed from the prewash by conventional methods.

Resin ion exchange is the reversible exchange of ions between a solid resin and a liquid. A variety of weak and strong base anion resins are effective in silver recovery. Using chloride as the mobile ion, the following is representative of the reaction:



The silver complex has a high affinity for the resin and consequently it is difficult to reclaim the silver and regenerate the resin. Recently, a concentrate has been developed that accomplishes this task economically. Other problems such as suspended matter, particularly gelatin, plugging the resin have also been solved by equipment design and operational procedures.

Reverse osmosis is a general separation technique. It involves a wastewater stream flowing under pressure through an appropriate porous membrane. Water passes through the membrane as product and the pollutants remain upstream from the membrane as concentrate. Reverse osmosis is governed by membrane surface phenomena and pore size, as well as wastewater characteristics. The membrane surface must be of such a chemical nature that it has a preferential sorption or repulsion for one of the constituents of the fluid mixture. Consequently, the membrane-liquid interface is enriched in one of the solution constituents. A continuous flow under pressure through the membrane capillaries results in a production solution (permeate) whose composition is different from that of the bulk solution. For recovery of silver from wash water by reverse osmosis, after-fix wash water is equalized, filtered, and then pumped through a reverse osmosis unit. Silver can be removed from the concentrate by conventional silver recovery methods depending on silver concentration and presence of other pollutants. Potential problems encountered with the use of reverse osmosis equipment for recovering silver from wash water are fouling of the membrane and biological growth. Proper maintenance and control are required to alleviate these problems. One plant reported difficulties with membrane fouling which required frequent replacement of the membrane with a resulting high maintenance cost. The problem was alleviated by the use of sand filtration in the waste stream prior to the reverse osmosis unit.

The low flow prewash system is a relatively new concept and is still being evaluated. This system concentrates most of the fix carryout in a low volume after-fix prewash tank. The system consists of segmenting the after-fix wash tank to provide a small prewash section with separate wash water make-up and overflow. The wash water flow can be optimized depending on the carryover silver concentration and the level of treatment. By design, the concentrations of fix, silver, and other chemicals reach high levels in the prewash tank under steady-state conditions. There is concern expressed by some investigators that this may cause problems with the quality of the processed material. In effect, the processed material receives additional fix time and exposure to potential contaminants while immersed in the prewash.

Dye stability tests, performed by one investigator on color paper processed using the prewash system, have shown an increase in yellow stain six months after processing. There is also a requirement for increased maintenance of the wash tank because of biological growth.

Coupler Recovery

The three color developers used in the K-14 color reversal process (DC) contain organic dye couplers. Since the couplers are in solution, it is common practice to recover these organic couplers from the waste developer overflow for economic reasons. The couplers are not recoverable from the IC process because they are not in solution. Instead, the color couplers are put into the three emulsion layers during manufacture of the film or paper and remain to form the color image after processing.

The (DC) couplers are soluble in the normally alkaline developers but will precipitate at neutral or acid pH. To recover the couplers, the pH of the waste developer is adjusted to 7 or less with sodium bisulfate and then the precipitated couplers are extracted by centrifugation. Carbon dioxide has also been used for pH adjustment. The photoprocessor may reuse the couplers in the appropriate developer solution. The recovery and reuse of couplers requires proper testing and quality control procedures to avoid problems with color balance and saturation in the processed films.

Bleach Regeneration

Bleaches are used in the black and white reversal process to dissolve the negative silver image and in the color process to oxidize the developed silver image to a silver halide which is subsequently dissolved in the fix solution. It is common practice in color processing to regenerate the reduced bleach for reuse by oxidizing the bleach back to its original state or by discharging a portion of the bleach and adding fresh chemicals to restore it to original specifications. The main active ingredient contained in color processing bleaches is either sodium or potassium ferricyanide, ferric EDTA, ferric chloride, or sodium

dichromate. A dichromate bleach is commonly used in black and white reversal processing and is not regenerated. Ferric chloride bleach is also not regenerated. The reuse of regenerated bleaches require various quality control measures, depending on the bleach type and regeneration method, to ensure against adverse effects in the product from improper chemical balance, chemical impurities, and dirt. These problems are addressed in more detail in a preceding subsection on product quality.

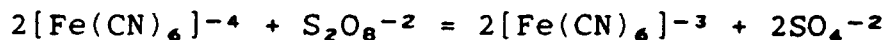
Ferricyanide Regeneration

The basis for all the ferricyanide regeneration methods is a sufficiently strong oxidizing agent that has reaction products compatible with or used in the process. Current regeneration processes which fulfill these requirements are:

- A. Persulfate regeneration
- B. Ozone regeneration
- C. Electrolytic bleach regeneration
- D. Miscellaneous chemical regeneration methods

Persulfate Regeneration--

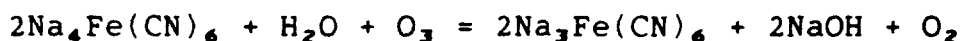
Persulfate regeneration is a batch process consisting of collecting the bleach overflow in a tank and adding potassium persulfate to oxidize the ferrocyanide ion back to ferricyanide by the following reaction:



Bromide is also added to replenish that taken up by the silver during bleaching. One problem with the persulfate method is a build-up of the sulfate ion which slows the bleaching action. To alleviate the problem, about 10 percent of the bleach is directly discharged before regeneration or the bleach drag-out rate in the process tank is regulated by squeegee adjustment so that a comparable sulfate reduction occurs.

Ozone Regeneration--

The use of ozone for ferricyanide bleach regeneration minimizes the salt build-up problems encountered with persulfate regeneration and reduces the need for bleach blowdown during regeneration cycling. The ozone process is characterized by the following reaction:



Stoichiometrically, 12.7 kg of sodium ferrocyanide are converted to 11.7 kg of sodium ferricyanide using 1.0 kg of ozone. Under varying conditions of pH, the ozone oxidation efficiency is near 100 percent for ferrocyanide concentrations above 1.0 gram per liter.

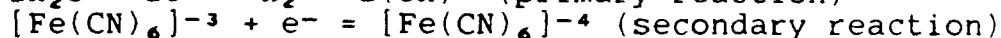
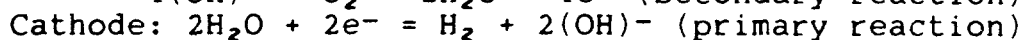
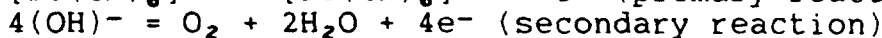
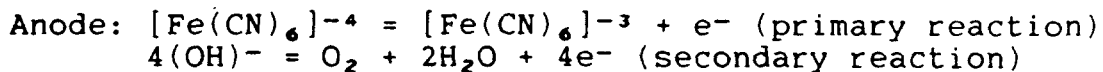
The pH of the bleach increases as the reaction proceeds, and bromide additions are required to replace the bromide taken up by the silver. Therefore, hydrobromic acid is added to accomplish both pH adjustment and bromide ion addition. Theoretically, one bromide ion is required for each ferrocyanide ion that is oxidized to ferricyanide. The hydrobromic acid avoids all build-up of sulfate and other unwanted by-products. If, in practice, there is a slight build-up of bromide ion, small amounts of sulfuric acid can be added for pH adjustment with little danger of high sulfate build-up.

Some photoprocessing plants have installed continuous in-line ozonation for ferricyanide bleach regeneration. This technique permits a significant reduction in the necessary ferricyanide concentration in the bleach tank, since the ferrocyanide level in the solution is kept low and the ferri to ferro ratio is the controlling factor in effective bleaching. With a lower ferricyanide bleach concentration, there is less drag-out and less pollution of the waste wash water.

Ozone can be somewhat hazardous because of its toxicity, but methods have been developed to use it safely. Safe practices include the use of ozone detectors to monitor the air in the vicinity of the ozonation tanks.

Electrolytic Regeneration--

Ferrocyanide can be oxidized to ferricyanide at the anode of an electrochemical cell. Because the reverse reaction occurs at the cathode, the cell must be divided by a semi-permeable membrane, or some other method of minimizing the cathode reaction must be employed. The electrolytic cell reactions are given below:



With improved cell technology minimizing the undesirable secondary reactions having become available recently, this method of ferricyanide bleach regeneration has found wider acceptance in the photoprocessing industry. Like ozonation, there is no requirement for bleach blowdown during the regeneration cycle.

Bromine and Peroxide Chemical Regeneration Methods--

Probably the simplest ferricyanide bleach regeneration technique, from a chemical point of view, is the use of bromine. The bromine performs the ideal role of oxidizing the ferrocyanide and replacing the bromide ions removed by the film as it passes through the bleach. It is an economical method, there are no unwanted reaction products, and there is minimal dilution. Because of the hazard and corrosiveness associated with the handling of liquid bromine, however, the method has not been widely accepted.

Bromate and bromite compounds have been used with satisfactory results and are somewhat easier to handle. The main reason for their not being used more widely has been hesitation by the industry to handle chemicals of this nature.

Hydrogen peroxide has also been used successfully. Hydrobromic acid is added to control pH and supply the required bromide ions. However, the problem of handling peroxide has restricted the use of this method.

Summary of Ferricyanide Bleach Regeneration Methods--

The most popular methods are persulfate and ozone regeneration. Both methods are efficient with the persulfate yielding about 90 percent of the used bleach for recycle and the ozone method allowing 100 percent recycle. Both methods require analytical monitoring of the regeneration process. The persulfate method consists of a single chemical addition requiring no special equipment beyond tanks and plumbing. It does have the problem of sulfate build-up which must be corrected by up to a 10 percent discharge. Ozonation allows essentially 100 percent recycle and is adaptable to continuous in-line regeneration but requires a larger investment in equipment and maintenance. Electrolytic regeneration is a relatively new method but appears to have advantages and disadvantages similar to ozonation.

Ferric EDTA Regeneration

Modifications in the processing of certain photographic materials have resulted in the substitution of ferric ions chelated with EDTA for ferricyanide as the bleaching agent. The ferric-EDTA bleach relies upon the oxidative power of the ferric ion which is reduced to ferrous ion in the process. Ferric EDTA is used alone as a bleach for certain color films and is used in combination with sodium or ammonium thiosulfate fixer for color paper processing. The combined material is known as bleach-fix.

Regeneration of the bleach involves the oxidation of the ferrous ion back to the ferric ion and the replenishment of various chemicals, principally bromide. Typically the oxidation process is performed as a batch process in a tank with aeration. Some plants aerate the bleach in the process bleach tank using compressed air which serves the dual purpose of solution agitation and oxidation.

Regeneration of the waste bleach-fix solution involves three steps. First, the silver must be recovered. Second, the reduced iron EDTA complex must be oxidized back to ferric EDTA. Finally, certain chemicals lost through carryover

with the film or paper must be added to bring the solution up to replenisher strength.

As with the desilvering of waste fixer solutions, there are several techniques available to remove the silver from bleach-fix waste. The most widely used technique is the silver recovery cartridge containing steel wool where the silver is replaced by iron, and the silver is retained in the cartridge. The metallic replacement method is most widely used both for economic and practical operating considerations. After passing the bleach-fix overflow through the silver recovery cartridge, the resulting solution is aerated to oxidize the ferrous EDTA complex to the ferric form. After aeration, the bleach is returned to a holding tank where make-up chemicals are added as required to restore the solution to replenishment strength.

It is also possible to use electrolysis to recover silver from bleach-fix baths. Equipment has recently appeared on the market which is designed for desilvering bleach-fixers electrolytically. This method has some advantages, such as better control of iron concentration and higher quality recovered silver, over metallic replacement, particularly in larger processing laboratories.

Irrespective of technique, it is possible to reuse between 70 and 80 percent of the bleach-fixers by regeneration. The 20 to 30 percent loss is due to a combination of carryout with the paper or film and excess bleach discharged to prevent contaminant build-up.

Reconstitution of Dichromate Bleach

Dichromate bleach is found in processes for motion picture color negative print film and in processes for black and white reversal film. The dichromate bleach used in color negative processing has the same function as the ferricyanide and EDTA bleaches, that is, it oxidizes the silver image to silver bromide. However, the function of the dichromate bleach used in black and white processing is to dissolve the silver image. To do this, the bleach formula contains no bromide and is very acidic. As a result the waste bleach contains silver. Before disposal of the

must be applied to prevent quality problems from biological growth, dirt accumulation, and inadequate washing.

Squeegees

Squeegees are devices designed to remove the liquid from the surfaces of film and paper as they move from one process tank to another to reduce solution carryover. They are placed at the exit of process solution and wash tanks where such placement is compatible with the process chemicals and emulsion. With proper placement and adjustment, squeegees conserve raw materials and reduce water use and replenishment volume (waste effluent). The amount of carryover reduction varies depending on a number of factors including squeegee type, process material area and machine speed, but typically ranges up to 95 percent. This reduction in carryover can result in a significant reduction of wash water. For example, the recommended wash water rate for the C-41 process without squeegee use is 183 l/sq m and with squeegee use is 91 l/sq m, a reduction of 50 percent.

Squeegee use is not universally applicable to all process machines, chemistry, or products. Proper placement, adjustment, and maintenance are extremely important to prevent physical quality problems from scratches and abrasions.

Among a wide variety of squeegee types, the most common are rubber or polyurethane wiper blades (usually used in pairs with the blades opposed to each other on opposite sides of the film or paper), air knives, Venturi, rotary buffer, and soft rollers. Wiper blades can have rigid mountings or, as more recently used, they are attached to the machine with plastic leaf springs which provide a constant self-adjusting blade pressure on the film. The air knife squeegee consists of slits cut into two opposed tubes from which air impinges on each side of the material at an angle of 20° to 45° off normal. The Venturi squeegee also utilizes air impingement where the material effectively becomes one side of a Venturi orifice. The rotary buffer consists of two opposed soft felt rollers rotating in opposition to the linear motion of the material. Soft rollers are used in opposing pairs. The roller has an inner shaft covered with a soft polyurethane

foam, which in turn is covered with a thin layer of silicone rubber having a very smooth surface. Soft roller squeegees are typically used for wide format materials. In addition to their squeegee action, the rollers aid in transporting the material through the machine and allow self threading which, in turn, means no leader is required.

Automatic Wash Water Controls

Excessive wash water flows can be avoided simply and effectively by the installation of automatic solenoid operated shutoff devices which completely stop the flow of water into the processor when it is not being used. A shutoff delay of a few minutes is needed so that time is allowed for removal of excessive chemical by-products carried into the wash water by the film. Further efficiencies can be accomplished by the installation of maximum flow regulation valves which prevent greater flow than needed.

Chemical Pre-Wash

After-fix wash water volume can be reduced by 60 to 70 percent with the addition of a salt bath between the fix and final wash. The role of the salt bath is to remove the fix from the emulsion chemically at a faster rate than can be done by washing. The salt bath provides a resultant reduction in washing time and water volume. A satisfactory bath of this type is a 20 grams per liter mixture of sodium sulfate and sodium bisulfite at a pH of 8 to 9.

Water Recycle

Wash water recycle has the potential for a significant reduction in a plant's water use. With effective application, along with other in-process controls, total plant process water use has been observed in actual applications to be reduced by about 70 percent. As discussed in the section on product quality, proper quality control is extremely important when recycling wash water. Wash water recycle is not necessarily applicable to all processes or practical in all plants because of product mix. When recycled water is used, the current practice is to

recycle the water to print processes and use fresh water for processing of originals so that in case of control problems irreplaceable originals are not damaged. Methods used for preparation of the water for recycle include treatment with resin ion exchange or reverse osmosis, which were described previously in the section on silver recovery from wash waters.

Housekeeping

The overall effectiveness of most of the previously discussed in-process controls is greatly reduced if a plant does not have a commitment to good housekeeping practices. The attendant results are a decreased economic benefit and increased pollutant loads.

For example, silver recovery units must be regularly maintained to prevent silver loss. The effluent from metallic replacement units must be carefully monitored and the units replaced when exhausted. The unit is usually considered to be exhausted when the effluent silver concentration is 1,000 mg/l as determined by the use of silver test paper or chemical analysis. Care must be exercised in the operation of electrolytic units to control cell current density to prevent sulfiding, if too high, and the loss of silver, if too low.

Plumbing leaks and the use of excess chemicals and water must be prevented to reduce hydraulic and chemical loads. The replenishment rate used should be the minimum required for proper process operation. The replenishment and wash water control valves should be calibrated and periodically checked for proper flow rate. Automatic control equipment should be used for cut-off of replenishment and wash water at the appropriate time at the start and end of a product run. Squeegees should be used at every solution exit where possible and should be regularly checked for proper squeegee action.

END-OF-PIPE TREATMENT TECHNOLOGIES

End-of-pipe treatment is the treatment of wastewater from a process just prior to discharge for the purpose of reducing

pollutant loads to the receiving stream. Although benefit may be gained from material recovery, the primary purpose is pollutant reduction. A number of establishments in the photographic processing industry use various types of end-of-pipe treatments.

In many cases the wastewaters are segregated into concentrated chemical wastes and wash water wastes and then treatments are applied to one or both waste streams. The size, complexity, and corresponding costs of the treatment equipment may be reduced by separation of wastewaters.

Descriptions of the end-of-pipe treatment technologies encountered in this industry follow.

Precipitation involves the reaction of two or more soluble chemicals to produce an insoluble product. This technique is used to reduce the amount of iron-cyanide complex being discharged by treating waste fix containing the complex with a flocculant and ferrous sulfate as a reducing agent. This results in the formation of insoluble ferrous ferrocyanide which settles with the aid of the flocculant. Sulfide precipitation is also used in a proprietary process for the reduction of metals such as silver, cadmium, lead, iron, and zinc from photoprocessing wastewater. Because these metals exist as complexes, it is necessary in some cases to break down the complex before effective precipitation can take place. This problem has been overcome by use of proprietary chemical additions.

Precipitation can be used for the reduction of chromium. As used in the electroplating industry, the amount of chromium in the wastewater is reduced by chemical reduction of hexavalent chromium to trivalent chromium and then precipitation of the chromium followed by filtration. The precipitation of chromium involves the addition of caustic soda or lime to the wastewater to increase the pH to 8-10. This decreases the solubility of the chromium, which precipitates as the hydroxide.

Cadmium can be precipitated as the hydroxide by adjustment of pH. Alkalinity has a significant effect on the solubility of cadmium. The theoretical solubility values of

cadmium hydroxide, according to Pourbaix, are approximately the following:

<u>pH</u>	<u>Solubility,</u> <u>mg/l</u>
8	3,000
9	30
10	0.03
11	0.003 (minimum)

The insolubility of cadmium carbonate suggests that precipitations with soda ash may reduce soluble cadmium to very low levels in effluent. Since many combined wastewaters contain some carbonate, it is very possible that cadmium carbonate rather than cadmium hydroxide is precipitated when wastewaters are neutralized with caustic or lime. Some reported values that seem unrealistically low for hydroxide precipitation actually may be achieved by this mechanism.

Cadmium sulfide is very insoluble (solubility product, $K = 10^{-29}$), so that a precipitation system based upon sulfides, combined with efficient removal of dissolved solids, may provide acceptable effluent.

Settling involves the concentration of particulate matter in wastewater by collecting the wastewater in tanks or ponds under quiescent conditions and allowing the suspended matter to settle with time. Waste streams in this industry do not normally contain large amounts of suspended solids; however, settling is commonly used in conjunction with precipitation to remove the resultant solids. Settling was observed to be used for (1) collection of precipitated ferrous ferrocyanide, (2) collection of precipitated metal sulfides, (3) reduction of suspended solids in aerated wastewater, and (4) preliminary settling of wastewater prior to discharge to a POTW.

Ozonation is a treatment process where ozone is bubbled through the wastewater. The wastewater is usually collected in tanks and the ozone added through sparging tubes in the bottom of the tank. Sometimes the wastewater is cascaded through two or more tanks connected in series. The ozone

provides a source of oxygen for oxidizable compounds and is used for the general reduction of BOD and COD in the wastewater. It is also used as a pretreatment for wastewater that is to be further treated by aeration. Plant 7781 has demonstrated that the addition of ozone prior to aeration enhances the effectiveness of the aeration process.

Filtration is used for reduction of waterborne suspended solids. It is accomplished by passing the wastewater stream through solid media such as retaining screens, cloths, or papers or through particulate media such as sand, gravel, carbon, or diatomaceous earth using gravity, pressure, or vacuum as the driving force. The filter equipment includes plate and frame presses, cartridges, and sand or mixed media beds. Filtration is employed to dewater precipitated ferrous ferrocyanide and metal sulfides and as a wastewater preconditioner prior to treatment by ion exchange or reverse osmosis. Diatomaceous earth filtration is used in the electroplating industry for reducing the amount of the previously precipitated chromium hydroxide in the treated wastewater.

Clarification is a unit operation for reduction of suspended solids. A clarifier is a tank with internal baffles, compartments, sweeps, and other directing and segregating mechanisms to separate the solids from the liquids. The solids are contained in the underflow, and the overflow consists of wastewater with reduced solids. Often the underflow, having a high solid content, is sent to a second clarifier or sent directly to a centrifuge or filter device for further concentration to sludge or cake solids. One facility was observed to use the clarifier as both a reaction vessel to precipitate ferrocyanide and as a clarifier to settle the precipitate from the liquid.

Aeration involves the treatment of wastewater with air to cause the reduction of oxygen demand. This is commonly done in ponds or large tanks. The aeration action is enhanced by pumping the wastewater into the air as a fountain or bubbling air through the water by means of sparging tubes in the bottom of the pond. Aeration is used to a limited extent in the Photographic Processing Industry for reduction of BOD and COD.

Neutralization involves the adjustment of the pH of a waste stream with acid or alkali to produce a near neutral condition. The most common method is to treat acidic streams with alkaline materials such as limestone, lime, soda ash, or sodium hydroxide. Alkaline streams are treated with acids such as sulfuric. There is no particular pH control problem in the industry. For example, developer wastes are alkaline and stop and fix wastes are acid. The combined wastes are often nearly neutral. Neutralization is employed at one plant to adjust the pH of wash water treated by reverse osmosis prior to discharge to a POTW.

Equalization involves the collection of wastewater in tanks or ponds for the purpose of equalizing or controlling the flow quantities prior to discharge or other treatment steps. Equalization is necessary and practiced prior to reverse osmosis.

Chlorination involves the addition of chlorine gas or a hypochlorite salt to the wastewater to cause breakdown of certain compounds by oxidation. It is used in the industry to reduce chlorine demand loads in cooperation with the local POTW and for control of slime organisms. It can also be used for odor abatement or as a specific reactant.

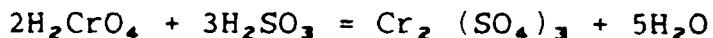
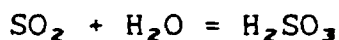
Flocculation is used to cause or accelerate the settling and concentration of suspended solids. Solids often settle slowly, or not at all, because of small size and electrical charge. Addition of flocculants such as alum, ferric chloride, and polymeric electrolytes promotes coagulation of particles and gives faster settling rates and improved separation. This process is used as an aid in the settling of precipitated iron-cyanide complexes.

Reverse Osmosis is a physical separation technique that involves a wastewater stream passing under pressure through a membrane. Water passes through the membrane as product (permeate) and the pollutants remain upstream from the membrane as concentrate. Reverse osmosis is used in the industry to reduce pollutants in the relatively dilute wash water wastes. This reduction of pollutants allows the recycle of the permeate and is practiced at several plants.

Evaporation is a technique that is used to reduce the volume of a wastewater stream. The one plant using this system recycled most of the processing chemicals and wash water to reduce the hydraulic load input to the evaporation system. The evaporation system consists of two stages of evaporation in a spray film evaporator with a third and final evaporation stage in a hot oil wiper film evaporator. Thermal energy is conserved by pre-heating the incoming water by directing it through the condensation tubes in the first evaporator and by storage of the wastewater between stages in thermally insulated tanks. The solids content of the wastewater is concentrated from 2 to 65 percent in the first two evaporation stages. The sludge remaining after the third stage of evaporation is about 85 percent solids. The evaporated water is condensed, purified, and reused in the process as wash water. The purification process, consisting of ion exchange, is necessary to remove ammonia compounds.

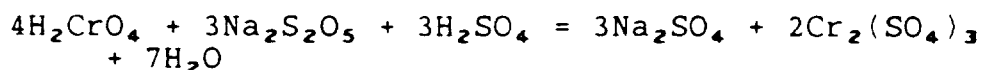
Chemical Reduction of Hexavalent Chromium - Chemical reduction is used for the treatment of wastewater by the electroplating industry for the reduction of hexavalent chromium to trivalent chromium. The reduction enables the trivalent chromium to be separated from solution by alkaline precipitation followed by diatomaceous earth filtration.

Reduction is a chemical reaction in which one or more electrons are transferred to the chemical being reduced from the reducing agent. Hexavalent chromium (CrVI) is usually reduced to trivalent chromium at a pH of 2 to 3 with sulfur dioxide (SO₂), sodium bisulfite, other sulfite-containing compounds, or ferrous sulfate. The reduction makes possible the removal of chromium as the trivalent hydroxide which precipitates under alkaline conditions. Typical reactions for SO₂ reduction are:

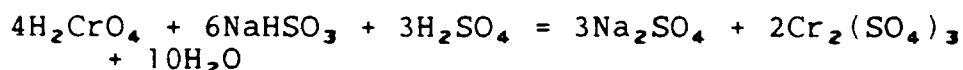


Representative reactions for reduction of hexavalent chromium under acid conditions using sulfite chemicals instead of SO₂ are:

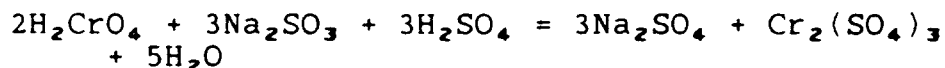
(a) sodium metabisulfite with sulfuric acid:



(b) sodium bisulfite with sulfuric acid:

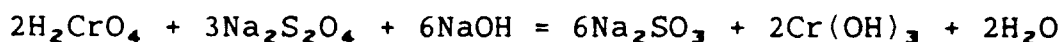


(c) sodium sulfite with sulfuric acid:



Reduction using sulfur dioxide is the most widely used method in the metal finishing segment of the electroplating industry, especially with larger installations. The overall reduction is readily controlled by automatic pH and oxidation-reduction potential instruments. Treatment can be carried out on either a continuous or batch basis.

Hexavalent chromium is also reduced to trivalent chromium in an alkaline environment using sodium hydrosulfite as follows:



Data from the specific plants employing these technologies are presented in Section V and their effectiveness is discussed in Section VII.

INDUSTRY CHARACTERISTICS

Information on the general characteristics of plants in the photographic processing industry has been collected in two industry surveys. The first, performed by the Eastman Kodak Company during the period 1969 through 1974, contains information on 237 plants. The results of this survey are summarized in Table III-4. Within a given category, e.g., method of waste disposal, the parts may add up to more than 100 percent. This is because in many cases more than one method of disposal may be used in a given plant. The totals

for each category do not necessarily equal 237 because some plants were unresponsive for some categories. The information included in this survey was collected from plants which had requested information from Kodak on waste disposal or effluent calculations. It is recognized that the information included in Table III-4 is six to eleven years old. Many of the processes in use at that time are obsolete, and it is likely that many of the individual plant characteristics have changed over this time period. Nevertheless, the data were valid at the time of the survey and can serve as a reference point for comparison with the more current information which follows.

A more recent survey conducted by EPA in the spring of 1977 is summarized in the following tables. Table III-5 correlates production and water use with the plant type, arranged by SIC code. SIC codes were not directly addressed in the telephone survey, rather the plant representative was asked what kind of customer the plant served. This information was used to place the plant in a SIC code using best available judgment. Tables III-6 to III-15 correlate various plant characteristics with production categories.

The 139 plants in this survey were contacted by telephone and asked questions according to a fixed format. The answers were recorded on a Telephone Survey Form, a blank sample copy of which is included in Appendix A. Prior to contacting the plant, a letter was sent to the plant explaining the purposes of the EPA program, and giving notification that they would be called and the type of information that would be requested. The list of plants contacted was compiled from trade magazine advertisements, membership directory of the Photographic Marketing Association (PMA), information supplied by the National Association of Photographic Manufacturers (NAPM), previous surveys, and personal contacts. The methods used to obtain plant lists tended to bias the selected plant sample towards relatively large plants [production greater than 93 sq m (1,000 sq ft) per day]. The information available at the time on the identity of the almost 10,000 smaller plants was insufficient for the selection of a random sample of the entire industry.

TABLE III-4

SUMMARY OF KODAK "200" PLANT SURVIVAL

METHOD OF WASTE DISPOSAL	Distribution of Plants by Water Use						
	TOTAL (237)*	up to					Unknown gal/day (26)
		1,000 gal/day (27)	1,000-10,000 gal/day (92)	10,000-50,000 gal/day (64)	over 50,000 gal/day (28)	(15)	
	(212)*	(25)	(83)	(60)	(28)	(9)	
Direct Discharge	6.1%	4 %	6 %	10 %	3.5%	0 %	
Municipal Sewer Pretreatment Prior to Municipal Sewer On-Site Treatment	83.5%	88 %	89 %	73.5%	96.5%	80 %	
	8 %	0 %	7.2%	6.7%	25 %	0 %	
	9 %	8 %	7.2%	21.7%	3.5%	20 %	
<u>SILVER RECOVERY</u>	(191)	(22)	(78)	(55)	(27)	(9)	
Metallurgical Replacement	66 %	50 %	75.7%	65.5%	66.7%	22 %	
Electrolytic	36 %	9.1%	23.1%	49.1%	74 %	22 %	
Other	5.2%	4.5%	3.4%	7.3%	3.7%	11 %	
None	5.8%	41 %	7.7%	0 %	0 %	45 %	
<u>BLEACH REGENERATION</u>	(179)	(5)	(79)	(54)	(27)	(7)	
Persulfate	55.8%	20 %	49.3%	74.2%	70 %	14.3%	
Ozone	1.7%	0 %	0 %	0 %	7.5%	14.3%	
Aeration	4.5%	40 %	2.6%	5.4%	0 %	14.3%	
None	42.5%	40 %	50.7%	25.8%	22.5%	71.4%	
<u>BLEACH-FIXER</u>	(72)	(4)	(35)	(22)	(9)	(2)	
Regeneration	85 %	50 %	80 %	95.5%	100 %	50 %	
No Regeneration	15 %	50 %	20 %	4.5%	0 %	50 %	

*Number of Photographic Processing Plants is Indicated in Parentheses

Data compiled during period 1969-1974.

III-64
86

TABLE III-4 (continued)

	TOTAL (237)*	Distribution of Plants by Water Use					Unknown gal/day (26)
		up to 1,000 gal/ day (27)	1,000-10,000 gal/day (92)	10,000-50,000 gal/day (64)	over 50,000 gal/day (28)		
<u>REUSE OF OTHER SOLUTIONS</u>							
Yes	16.7%	0 %	5.1%	18.5%	64 %	0 %	
No	83.3%	100 %	94.9%	81.5%	36 %	100 %	
<u>REUSE OF WASH WATERS</u>							
Yes	5.7%	5 %	2.5%	13 %	13 %	0 %	
No	94.3%	95 %	97.5%	87 %	87 %	100 %	
<u>USE OF SQUEEGERS</u>							
Yes	63.2%	37.5%	65 %	64.3%	86 %	0 %	
No	36.8%	62.5%	35 %	35.7%	14 %	100 %	
<u>WASH WATER CONTROLS</u>							
Yes	41 %	40 %	27 %	44.5%	61.5%	0 %	
No	59 %	60 %	63 %	55.5%	38.5%	100 %	
<u>BOD₅ LOADING (lbs/day)</u>							
10	22.5%	88.5%	16.6%	1.6%	0 %	54.6%	
10-100	48.9%	11.5%	79 %	45.2%	3.7%	36.4%	
100-500	21.1%	0 %	4.4%	43.5%	59.3%	4.5%	
500	7.5	0 %	0 %	9.7%	37 %	4.5%	

*Number of Photographic Processing Plants is Indicated in Parentheses

III-65
87

TABLE III-5

CORRELATION OF TYPE OF SERVICE WITH PRODUCTION AND WATER USE
FROM TELEPHONE SURVEY INFORMATION

Type of Service	Production*					Total	Water Use**					Total
	1	2	3	4	5		1	2	3	4	5	
SIC 7221 Portrait Studio	1	1	2	1	0	5	0	3	2	0	0	5
SIC 7333 Commercial Industrial (X-ray, Aerial) Publishing	8	2	8	2	2	22	6	5	8	3	0	22
	10	1	3	0	0	14	8	2	2	0	2	14
	0	0	0	1	1	2	0	0	1	0	1	2
SIC 7395 Amateur Professional Military Government	10	6	47	9	9	81	7	15	48	9	2	81
	11	3	15	3	3	35	4	12	15	2	2	35
	2	0	0	0	0	2	2	0	0	0	0	2
	1	3	1	0	0	5	1	3	1	0	0	5
SIC 7819 Movie, TV	0	2	2	4	0	8	0	1	2	4	1	8
Unknown	1	0	0	1	0	2	0	1	0	0	1	2
Totals	44	18	78	21	15	176***	28	42	79	18	9	176***

* Production key

- 1 = less than 1,000 sq ft per day
- 2 = 1,000 to 2,999 sq ft per day
- 3 = 3,000 to 20,000 sq ft per day
- 4 = greater than 20,000 sq ft per day
- 5 = unknown

** Water Use key

- 1 = less than 1,000 GPD
- 2 = 1,000 to 9,999 GPD
- 3 = 10,000 to 100,000 GPD
- 4 = greater than 100,000 GPD
- 5 = unknown

*** Total number of plants greater than 139 caused by double accounting, i.e., a plant fits into more than one category.

1118
88

TABLE III-6

CORRELATION OF PRODUCTION WITH WATER USE FROM TELEPHONE SURVEY INFORMATION

Production Category, sq ft/day	Water Use Category, gal/day					Total
	Less than 1,000	1,000 to 9,999	10,000 to 100,000	More than 100,000	Unknown or not given	
Less than 1,000	19	11	2	0	3	35
1,000 to 2,999	3	11	3	0	0	17
3,000 to 20,000	2	9	42	4	1	58
More than 20,000	0	0	4	10	2	16
Unknown or not given	0	2	9	0	2	13
Totals	24	33	60	14	8	139

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TABLE III-7

CORRELATION OF PROCESS TYPE WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Black and White Only	Color Negative Only	Color Reversal Only	Color Negative and Reversal	Color and Black and White	Totals
Less than 1,000	16	5	0	1	13	35
1,000 to 2,999	5	5	0	0	7	17
3,000 to 20,000	2	2	7	10	37	58
More than 20,000	0	1	0	2	13	16
Unknown	<u>0</u>	<u>6</u>	<u>0</u>	<u>1</u>	<u>6</u>	<u>13</u>
Totals	23	19	7	14	76	139

HH
68
25

TABLE III-8
CORRELATION OF PROCESSING METHODS WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Machine Processing	Manual Processing	Both Machine and Manual Processing	Totals
Less than 1,000	21	4	10	35
1,000 to 2,999	14	1	2	17
3,000 to 20,000	56	0	2	58
More than 20,000	15	0	1	16
Unknown	<u>11</u>	<u>0</u>	<u>2</u>	<u>13</u>
Totals	117	5	17	139

TABLE III-9

CORRELATION OF REPLENISHMENT USE WITH PRODUCTION
FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Used	Not used	Totals
Less than 1,000	32	3	35
1,000 to 2,999	15	2	17
3,000 to 20,000	57	1	58
More than 20,000	16	0	16
Unknown	<u>13</u>	<u>0</u>	<u>13</u>
Totals	133	6	139

TABLE III-10

CORRELATION OF SQUEEGEE USE WITH PRODUCTION
FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Everywhere Recommended	Partial	Not Used	Totals
Less than 1,000	11	9	15	35
1,000 to 2,999	10	3	4	17
3,000 to 20,000	52	3	3	58
More than 20,000	16	0	0	16
Unknown	<u>12</u>	<u>1</u>	<u>0</u>	<u>13</u>
Totals	101	16	22	139

TABLE III-11

CORRELATION OF SILVER RECOVERY USE WITH PRODUCTION
FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	From All Fix Solution Overflows	From Portion of Overflows	Not Used	Totals
Less than 1,000	27	2	6	35
1,000 to 2,999	16	1	0	17
3,000 to 20,000	57	1	0	58
More than 20,000	16	0	0	16
Unknown	<u>13</u>	<u>0</u>	<u>0</u>	<u>13</u>
Totals	129	4	6	139

~~III-72~~
94

TABLE III-12
CORRELATION OF SILVER RECOVERY METHODS WITH PRODUCTION FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	Metallic Replacement	Electro- lytic	Both Metallic Replacement and Electrolytic	Metallic Replacement and/or Electrolytic and Ion Exchange (resin)	Off Site		Totals
					Off Site	None	
Less than 1,000	9	12	5	0	3	6	35
1,000 to 2,999	7	6	4	0	0	0	17
3,000 to 20,000	15	18	24	0	1	0	58
More than 20,000	0	10	4	2	0	0	16
Unknown	<u>6</u>	<u>1</u>	<u>6</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>13</u>
Totals	37	47	43	2	4	6	139

~~III-12~~
95

TABLE III-13
CORRELATION OF BLEACH REGENERATION USE WITH PRODUCTION
FROM TELEPHONE SURVEY INFORMATION

Production, sq ft/day	All Bleach Solutions	Portion of Bleach Solutions	Bleaches Used		Totals
			But Not Regenerated	No Bleaches Used	
Less than 1,000	8	5	6	16	35
1,000 to 2,999	9	3	0	5	17
3,000 to 20,000	38	16	2	2	58
More than 20,000	15	0	1	0	16
Unknown	<u>10</u>	<u>2</u>	<u>1</u>	<u>2</u>	<u>13</u>
Totals	80	26	10	23	139

~~III-74~~
96

TABLE III-14

CORRELATION OF TREATMENT USE WITH PRODUCTION
FROM TELEPHONE SURVEY INFORMATION

Production sq ft/day	Precipi- tation	Settling	Ozonia- tion	Fil- tration	Clarifi- cation	Aeration Pond	Neutrali- zation	Equali- zation	Chlorin- ation	Ion Exchange	None	Not Given	Totals
Less than 1,000	0	1	0	1	0	0	0	0	0	0	33	0	35
1,000 to 2,999	0	1	0	0	1	0	1	0	0	0	14	0	17
3,000 to 20,000	4	3	1	1	1	0	2	1	1	0	43	3	60
More than 20,000	3	0	1	0	0	1	1	0	0	1	7	3	17
Unknown	0	0	0	0	0	0	0	0	0	0	13	0	13
Totals	7	5	2	2	2	1	4	1	1	1	110	6	142*

* Total number of plants greater than 139 indicates double accounting.

97

TABLE III-15

CORRELATION OF DISCHARGE METHOD WITH PRODUCTION
FROM TELEPHONE SURVEY INFORMATION

Production sq ft/day	POIW	Direct	Separated Waste Streams Both POIW and Direct	POIW and Contract Haul	Percolation- Evaporation Pond	Unknown	Totals
Less than 1,000	29	3	0	1	1	1	35
1,000 to 2,999	16	1	0	0	0	0	17
3,000 to 20,000	53	2	1	1	0	1	58
More than 20,000	10	1	1	1	0	3	16
Unknown	<u>10</u>	<u>0</u>	<u>1</u>	<u>1</u>	<u>0</u>	<u>1</u>	<u>13</u>
Totals	118	7	3	4	1	6	139

98

SECTION IV

INDUSTRY CATEGORIZATION

INTRODUCTION

The purpose of industry categorization is to establish subcategory groupings for pollution control purposes within the photographic processing industry such that plants within each group have an equal ability to meet the established effluent limitations guidelines. Upon examination of the various categorization bases it was determined that this industry should be considered as a single group. The following subsection describes the considerations for making this determination.

CATEGORIZATION BASIS

After considering the nature of the various segments of the photographic processing industry and the operations performed therein, the following factors were considered as bases for subcategorization:

1. Process type
2. Service performed or customer type
3. Type and quantity of material processed
4. Age of facility and number of employees
5. Geographic location
6. Water use
7. Effluent discharge destination

Process Type

Since the processes performed in a plant are the sources of wastes from a plant, the photographic processes would seem to be a natural candidate for subdividing the industry. As described in Section III, there are a number of process types used.

Many of the plants surveyed use multiple process types for processing a mixture of photographic materials. The mixed wastes from these plants tend to blend any distinguishing process characteristics. There are, of course, plants where

wastes do not contain all of the pollutant parameters of concern because only one process type is used or the process blend is such that one or more of the waste parameters of concern is omitted. For example, a black and white negative only plant does not use bleach, and a color negative only plant typically does not use ferricyanide or dichromate bleach. (The color negative process, MC-42, uses ferricyanide bleach, but observations during the study showed a tendency for color negative and print plants to use the C-41 process which uses a ferric EDTA bleach. The MC-42 process is more likely to be used in plants having a mix of reversal processes and use a house ferricyanide bleach system.) As a result, total cyanide and chromium pollutants are not added to the wastewater and these plants will have no difficulty in meeting any limitation on these pollutant parameters. Therefore, the presence or absence of certain process types is not a basis for subcategorization.

Service Performed or Customer Type

The service performed or customer type determines the types of materials to be processed which, in turn, determines the processes utilized. Therefore, the above discussion about process type is also applicable to the service performed.

Type and Quantity of Material Processed

Some distinguishing process characteristics for the various material types are shown in Table IV-1.

TABLE IV-1
Distinguishing Process Characteristics of Various
Material Types

<u>Material Type</u>	<u>Processing Characteristics</u>
Black and White Negative	No bleach
Reversal	Dichromate bleach, waste bleach contains silver
Color Film Negative	High silver, ferricyanide or EDTA bleach
Reversal	High silver, ferricyanide, EDTA, or ferric chloride bleach
Negative, movie	High silver, ferricyanide bleach
Negative, movie print	Low silver, dichromate or ferricyanide bleach
Color Paper Negative	Low silver, EDTA bleach
Reversal	Low silver, EDTA bleach

As indicated, some of the materials have a relatively high or low amount of silver in the emulsion that is potentially released to the wastewater. Generally, most plants process a mixture of materials which tend to produce an amount of silver in the effluent per production unit that is in the mid-range of silver that would come from film or paper alone. For example, it is common for a plant to process both film (high silver) and paper (low silver). Even a movie film plant which processes all film is analogous to the common film-paper plant in that the movie plant processes both high silver content negatives and low silver print film. A plant which processes only reversal films will have a relatively high silver load prior to silver recovery. Silver recovery processes are generally operated to reduce silver concentrations to comparable levels regardless of the silver concentration before silver recovery. So, assuming similar hydraulic loads, a reversal only plant would potentially have effluent silver levels equivalent to those of other types of plants.

The bleach characteristics in Table IV-1 are related to process type; therefore, the discussion on process types is applicable.

Production normalized quantities of process water and silver in the effluent versus the quantity of material processed (production) are shown in Figures IV-1 and IV-2, respectively, for the plants studied. The plants having end-of-pipe treatments are identified in Figure IV-2.

The water use plot indicates no strong dependency of water use with production, and the plot of silver load versus production shows a general downward trend of lower silver with increased production. However, when considering the grouping of plants with similar silver treatment, the grouped silver quantities are generally independent of production. The downward trend is most likely a result of increased silver treatment rather than a dependency on production. Water use may be higher in plants with production of less than 93 sq m/day (1,000 sq ft/day) due to inefficiencies of operation and the use of less efficient (in terms of water use) process equipment, but the available information is insufficient to make this determination. Therefore, based on available information, processed material quantity is not a suitable parameter for subcategorization.

Age of Facility

Production normalized quantities of process water versus plant age and silver in the effluent versus plant age are shown in Figures IV-3 and IV-4, respectively, for the plants studied. No particular relationship between these parameters is shown, and therefore plant age is not a suitable basis for subcategorization.

Number of Employees

Production normalized quantities of process water versus number of employees and silver in the effluent versus number of employees are shown in Figures IV-5 and IV-6, respectively, for the plants studied. No particular relationship between these parameters is shown, and therefore number of employees is not a suitable basis for subcategorization.

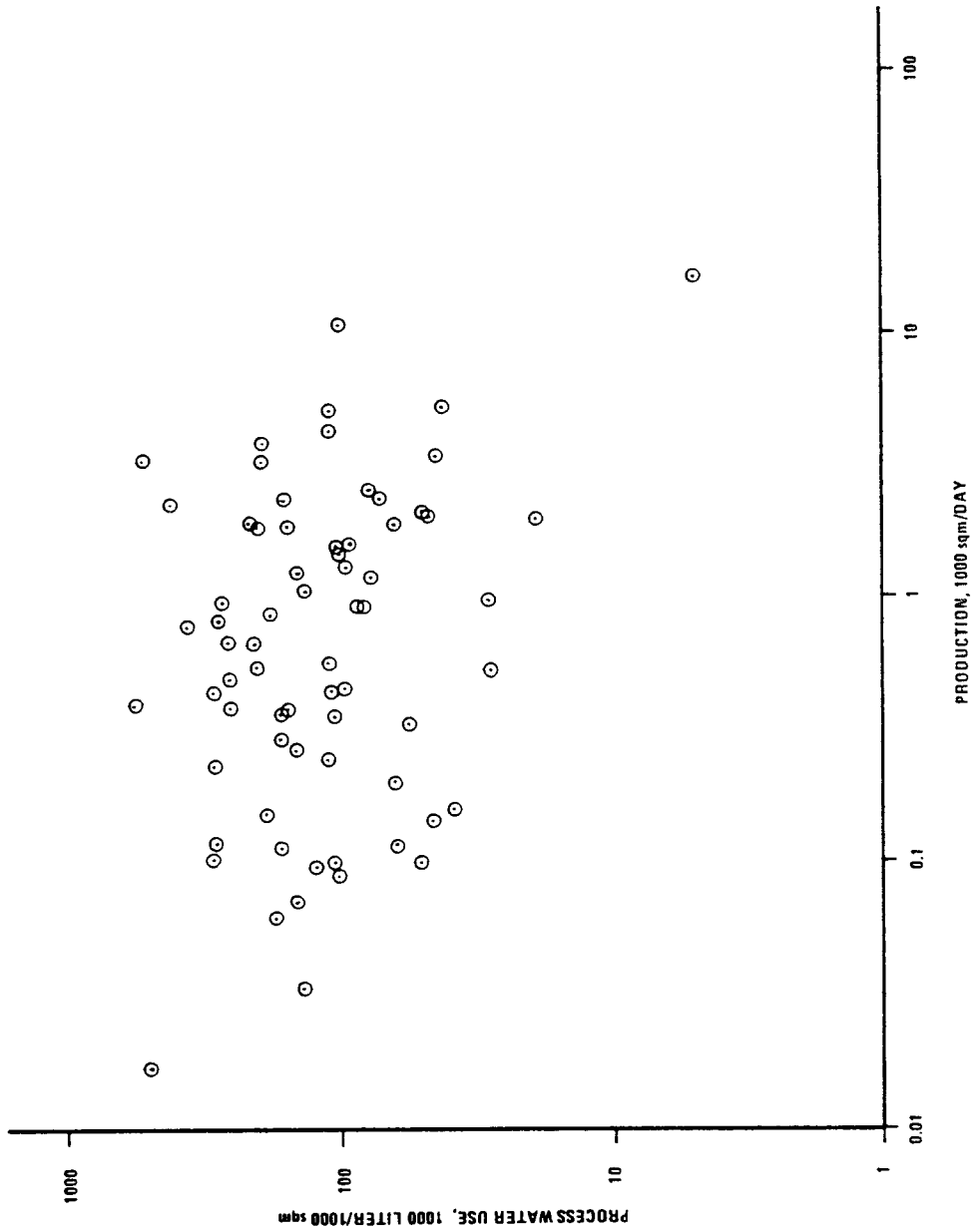


FIGURE IV-1 PROCESS WATER USE VS. PRODUCTION

~~IV-5~~
103

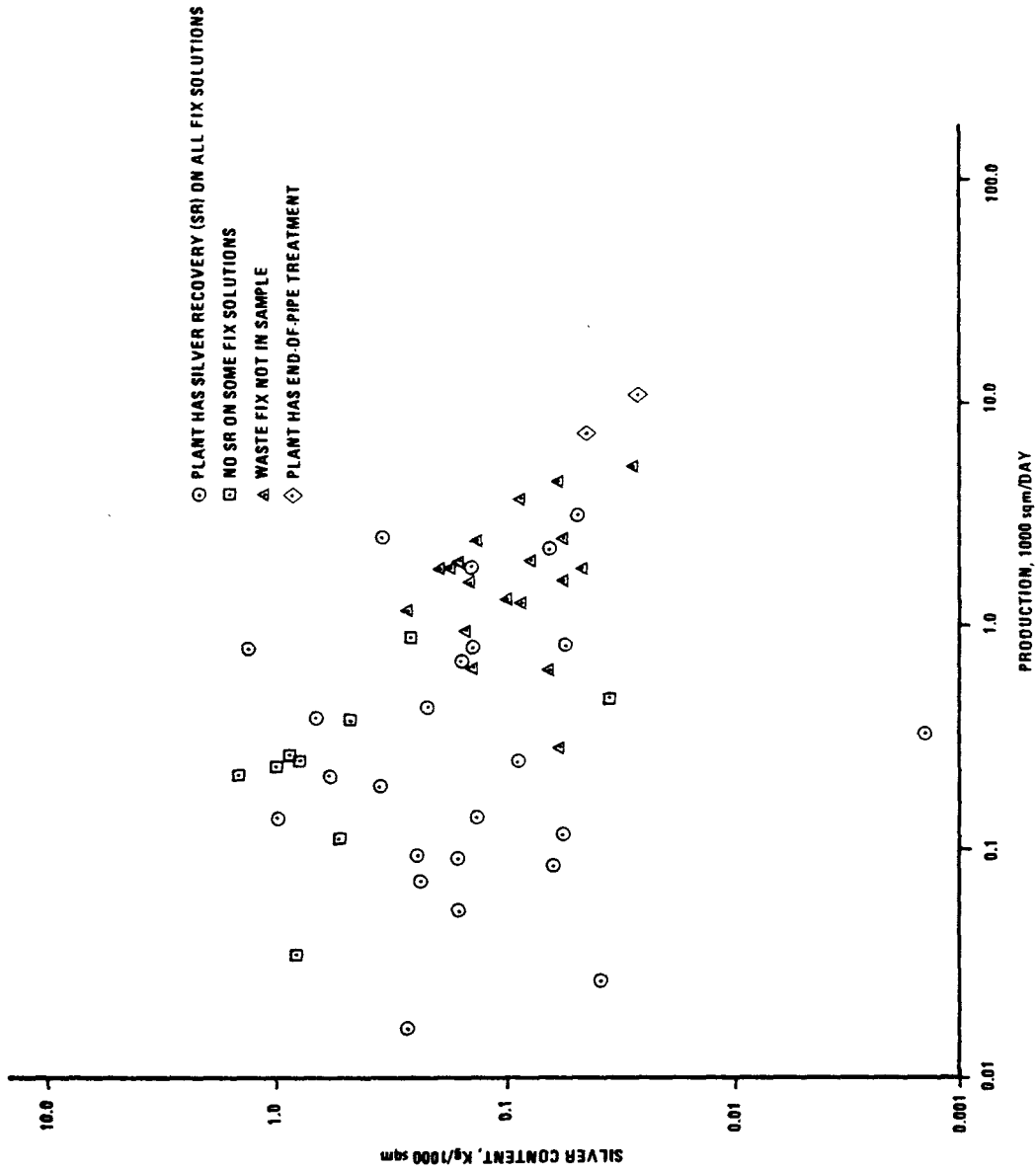


FIGURE IV-2 AMOUNT OF SILVER IN EFFLUENT VS. PRODUCTION

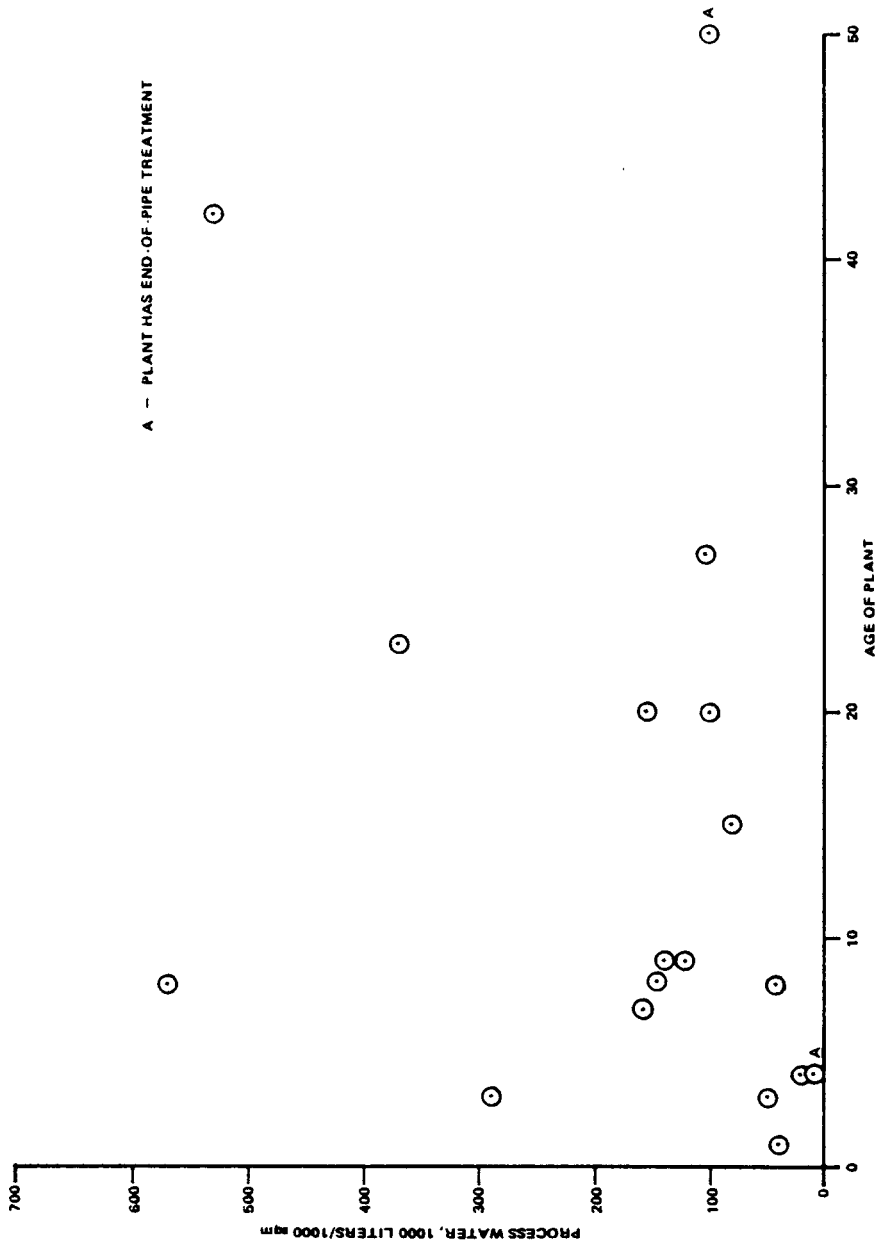


FIGURE IV-3 AGE OF PLANT VS. PROCESS WATER USE

IV-7
105

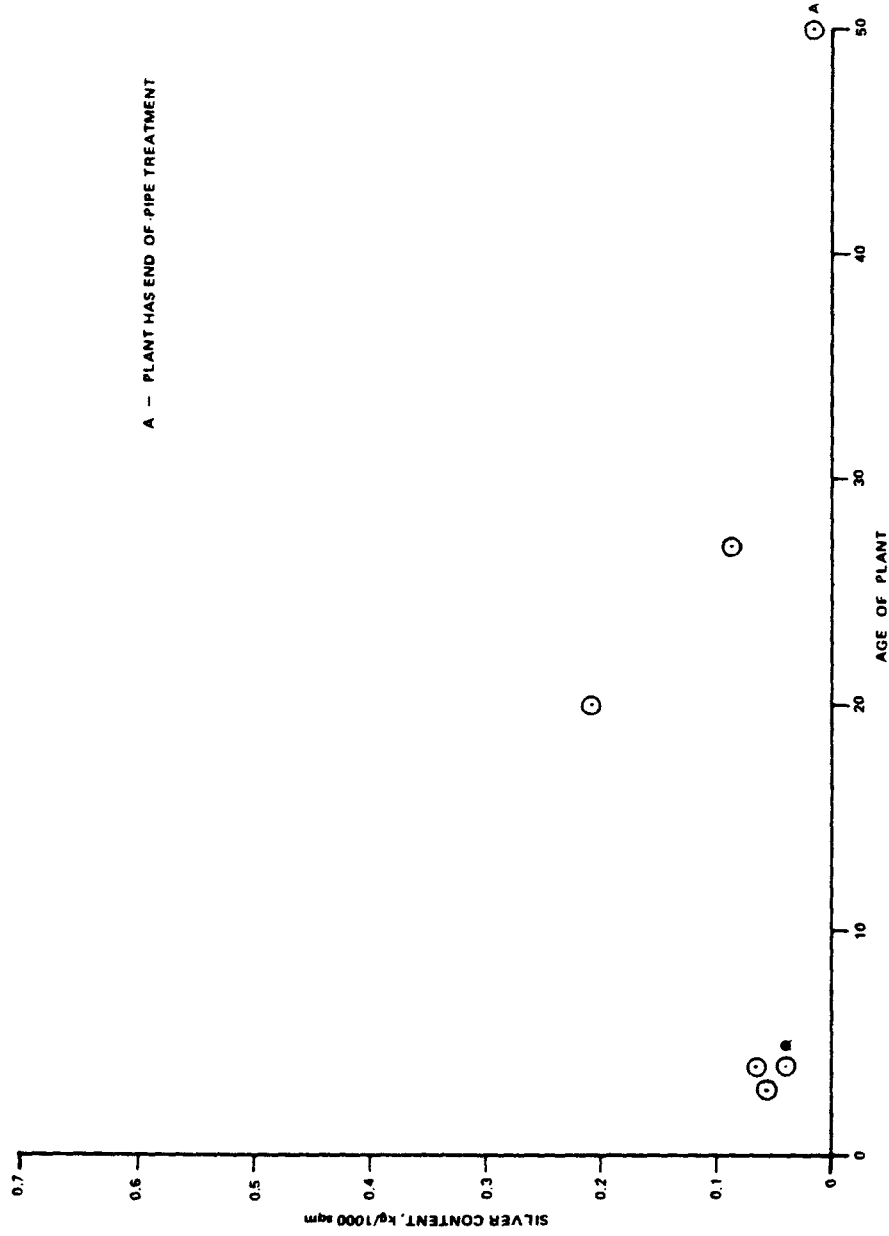


FIGURE IV-4 AGE OF PLANT VS. AMOUNT OF SILVER IN EFFLUENT

106
B-A-1

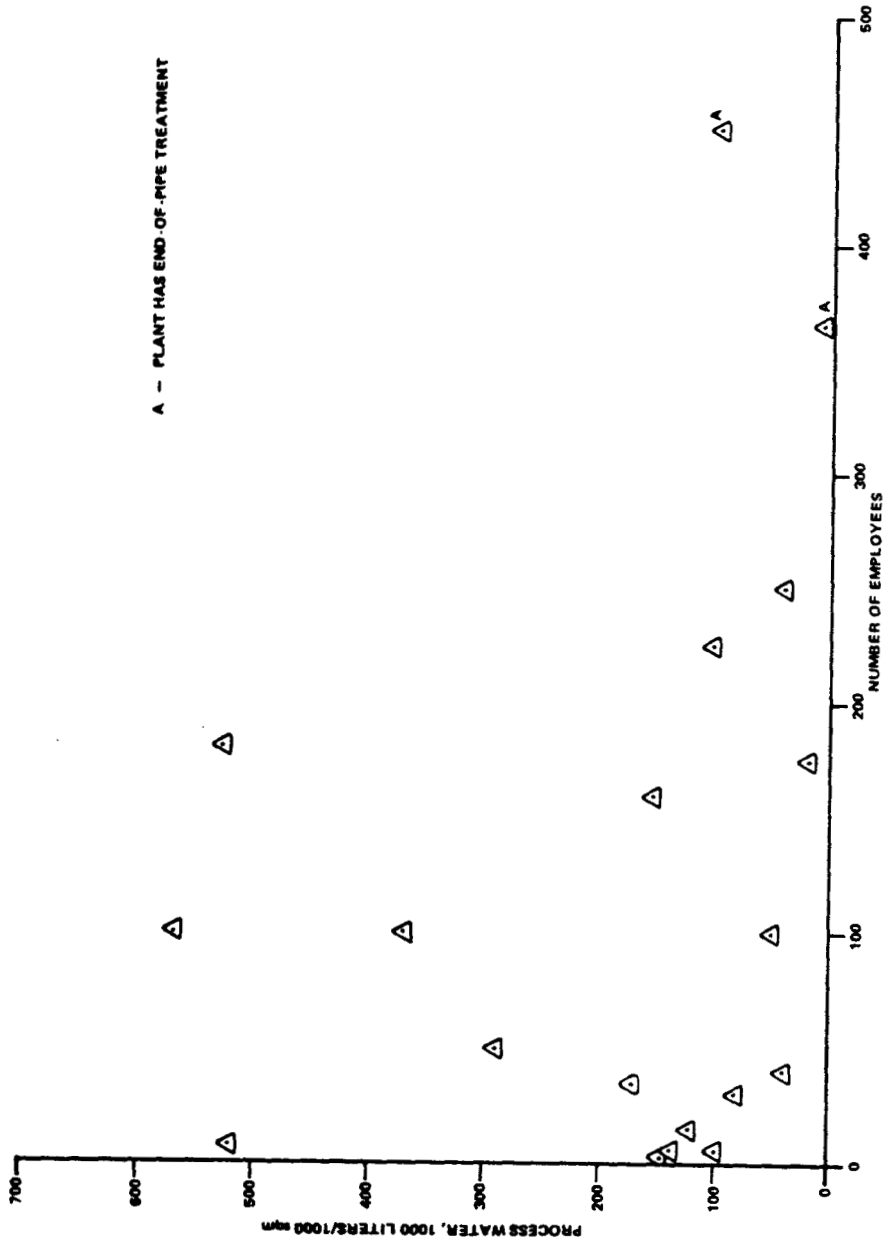


FIGURE IV-5 NUMBER OF EMPLOYEES VS. PROCESS WATER USE

IV-9
707

A - PLANT HAS END-OF-PIPE TREATMENT

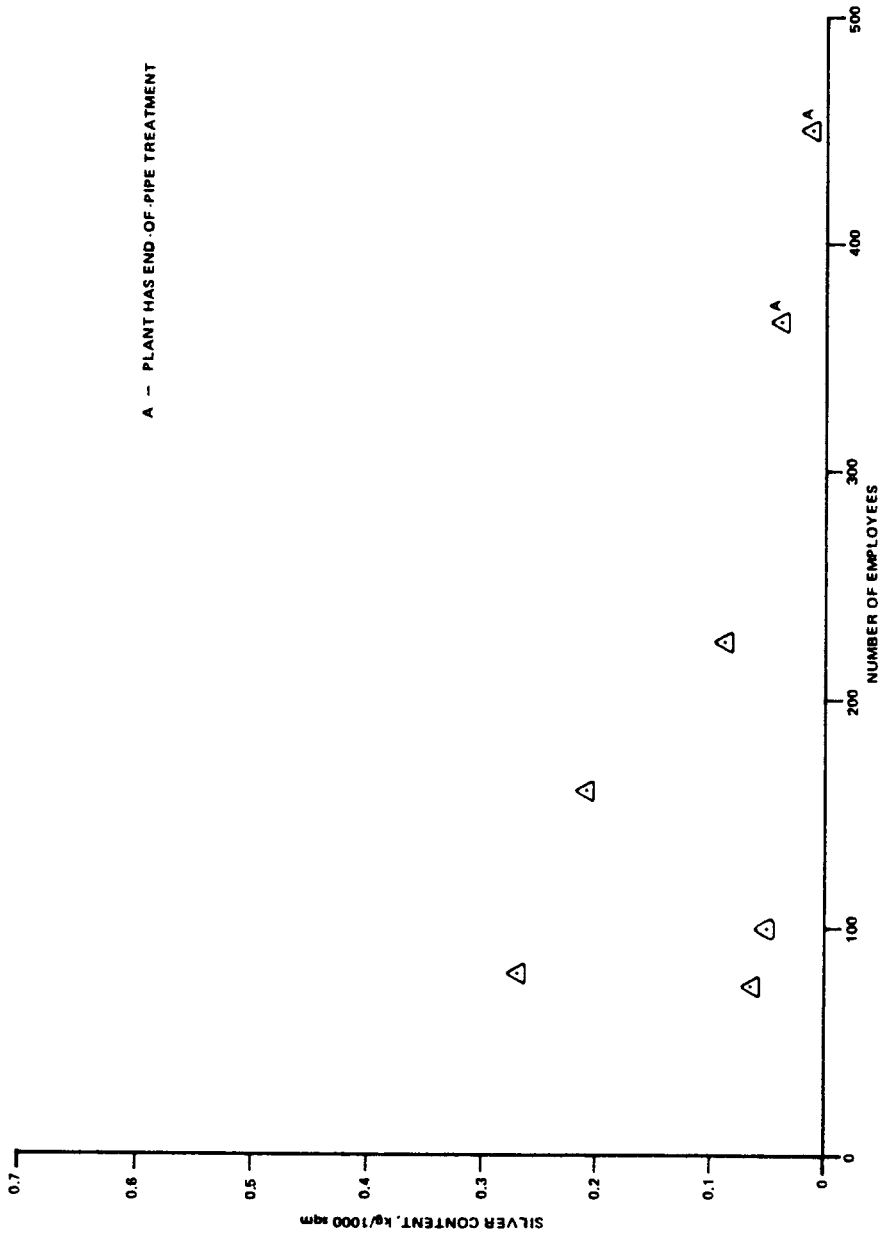


FIGURE IV-6 NUMBER OF EMPLOYEES VS. AMOUNT OF SILVER IN EFFLUENT

IV 10
108

Geographic Location

Geographic location is not a basis for subcategorization. Photographic processes are not affected by the physical location of the facility. The price or availability of water may affect the amount of modification to procedures used in each plant. However, procedural changes to conserve water can affect the concentration of pollutants discharged but not the amount or characteristics of the constituents. The waste treatment procedures described in Section III can be utilized in any geographical area. In the event of a limitation in the availability of land space for constructing a waste treatment facility, the in-process controls and wash water conservation techniques described in Section III can be adopted to minimize the land space required for the end-of-process treatment facility. Often, a compact package unit can easily handle end-of-process waste, if good in-process techniques are utilized to conserve raw materials and water.

Water Use

As previously shown in Figure IV-1, no strong dependency exists between water use and plant size in terms of the quantity of material processed. It is expected that the relative amount of water used by very small plants, less than 93 sq m/day (1,000 sq ft/day), will be larger than the industry norm due to inefficiencies of operation. For example, when production is low, process machines may be on stand-by for long periods during which time there is some wash water flow. Small processors commonly use manual tray processing and low volume production sheet film and paper processors which are inherently less efficient in water use than large continuous process machines. The available data are insufficient to quantify the water use for these very small plants. For the size of plants represented in Figure IV-1, there is no basis for subcategorization.

Effluent Discharge Destination

Of the approximately 11,000 photographic processing dischargers, fewer than 20 are direct dischargers as determined by an NPDES permit search. The fact that a plant is a direct discharger has no effect on the type of pollutants discharged. Direct dischargers may currently

have more stringent limitations because of permit requirements. As a result, they may have applied more effective controls and thus have smaller pollutant amounts than those which discharge to POTWs. The available data are insufficient to make this determination.

SELECTION OF PRODUCTION RELATED PARAMETER

In the selection of a suitable production normalizing parameter, a number of production related factors were considered. The level of production activity in a particular plant can be expressed as the processed area, raw materials consumed, number of process machines, or number of employees.

All of these parameters have some relation to the level of production in a particular plant, but area processed is more closely associated with the level of activity relative to pollutant discharge than the other parameters for the photographic industry. Raw material consumed is directly related to area processed but with the area being the primary factor. The number of process machines is related to the area processed but varies depending upon the degree of utilization of each machine in a particular plant. The number of employees is an unreliable measure of production because of a varying degree of automation, particularly in the smaller facilities. Therefore, the area of emulsion processed was selected as the production normalizing parameter.

SECTION V

PROCESS WASTE CHARACTERIZATION

DATA BASE

The initial EPA study of the Photographic Processing Industry was conducted during the period mid-1974 through mid-1976 and included a Kodak "200 plant" survey and the collection of data and sampling of three plants in the fall of 1974. In the spring of 1976 the National Association of Photographic Manufacturers (NAPM) conducted a sampling effort of 37 plants. An expanded EPA effort was initiated in the fall of 1976 for the purpose of collecting additional information. This second EPA study began in October 1976 with the sampling of two plants. Then information was obtained from 139 plants in a telephone survey which was described in Section III. A formal request for data was made to those plants which indicated during the telephone survey that they had available self-monitoring data on wastewater characteristics. A total of 19 plants submitted some information based on this request. From information gathered in the telephone survey, twenty plants were selected and visited. Detailed engineering information was obtained on the process water use, in-process controls, end-of-pipe treatments and wastewater characteristics. The factors considered during the selection process were product mix, in-process controls, end-of-pipe treatments, size (production) and data availability. Primary consideration was given to the use of end-of-pipe treatments and in-process controls. Five of the 20 plants visited were selected for sampling by EPA. Selection factors considered were product mix, in-process controls and end-of-pipe treatments. The sampling of these plants took place in the summer of 1977. A summary of these data sources is given below:

~~V-1~~
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<u>Information Source and Type</u>	<u>Number of Plants</u>
1969-1974 Kodak "200 Plant" Survey	237
1974 - EPA Engineering Plant Visit and Sampling	3
1976 - NAPM Sampling	37
1976 - EPA Sampling	2
1976 - EPA Telephone Survey	139
1976 - EPA Engineering Plant Visit	20
1977 - EPA Sampling	5
1976 - Self-monitoring data submitted to EPA on request	17

Note that some plants in each source category may be included in another category. For example, some of the 37 plants in the NAPM sampling effort were also covered in the 139 plant telephone survey.

Section V contains data for 76 plants obtained from the described sources of information. Four digit number codes are used to represent each of the studied plants. The series of numbers 02nn have been assigned to the 37 plants included in the 1976 NAPM sampling effort. The data have been condensed (by averaging) and abridged. Table V-1 lists the plants studied by plant code and gives some general characteristics of their customer type, SIC code, relative size, and production. The production information is given in terms of percent film production, percent black and white production, and the percentage of color production attributed to the several bleach types.

Sampling Efforts

EPA conducted waste stream sampling efforts in the fall of 1974 and 1976 and in the summer of 1977. A major portion of the 1977 effort was devoted to the sampling and analyses for priority pollutants. The collected effluent samples consisted of flow proportioned composites taken during single process days in the 1974 and 1976 sampling efforts. Flow proportioned composites were taken for each of three days at each site during the 1977 sampling effort with the exception of plants 2714 and 9026. No effluent samples were

TABLE V-1
PRODUCTION SUMMARY

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
0021	AM	7395	C	0	15	1	99	0
0045	AM	7395	B	8	14			0
0118	COM	7333	C	0	40	15	85	0
0201	"	"	A	0	"	11	89	0
0202	AM-PRO	7395	<A	0	"	0	100	0
0203	AM	7395	A	"	"	0	"	0
0204	AM	7395	C	"	"	1	"	0
0205	MOV	7819	C	"	"	15	"	"
0206	AM-PRO	7395	B	0	"	0	100	0
0207	PRO	7395	A	0	"	0	100	0
0208	AM	7395	C	0	"	"	"	0
0209	AM-PRO	7395	A	"	"	0	"	0
0210	SCH	7221	B	0	"	1	99	0
0211	AM-PRO	7395	A	0	"	0	0	0
0212	AM	7395	<A	0	0	0	100	0
0213	"	"	B	"	"	0.3	"	0
0214	AM	7395	<A	0	"	0	100	0
0215	AM	7395	C	"	"	1	"	0
0216	AM	7395	<A	"	"	0	"	0
0217	AM	7395	C	"	"	1	"	0
0218	AM	7395	B	"	"	2	"	"

* All percentages are percent of total production
 " Not given and/or cannot be estimated from processes used

CUSTOMER KEY:

AM - Amateur
 AER- Aerial
 COM- Commercial
 GOV- Government
 MIL- Military
 MOV- Movie
 PMS - Portrait Studio
 PRO - Professional
 SCH - School
 X-R - Industrial X-Ray

SIZE KEY: Production, sq m/day (sq ft/day)

<A <93 (<1,000)
 A 93-186 (1,000-2,000)
 B 186-464 (2,000-5,000)
 C 464-4,640 (5,000-50,000)
 D 4,640-∞ (50,000-∞)

V-3
113

TABLE V-1
(continued)

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
0219	AM	7395	C	α	α	2	α	α
0220	α	α	A	0	α	0	100	0
0221	MOV	7819	B	0	100	α	0	0
0222	AM	7395	B	0	α	α	α	0
0223	AM	7395	C	0	α	0.3	α	0
0224	α	α	A	0	α	0	100	0
0225	AM	7395	C	α	α	α	α	α
0226	AM	7395	A	0	α	0	100	0
0227	MOV	7819	B	α	100	22	α	α
0228	MOV	7819	C	0	100	1	α	α
0229	α	α	<A	α	α	5	α	α
0230	AM	7395	B	α	α	α	α	0
0231	MOV	7819	C	0	100	α	0	α
0232	AM	7395	C	0	100	100	0	0
0233	AM	7395	C	0	100	100	0	0
0234	AM	7395	C	0	100	100	0	0
0235	AM	7395	C	0	100	100	0	0
0236	AM	7395	C	0	100	100	0	0
0237	AM	7395	C	0	100	100	0	0
0662	AM	7395	C	0	15	1	99	0

* All percentages are percent of total production
α Not given and/or cannot be estimated from processes used

SIZE KEY: Production, sq m/day (sq ft/day)

<A	<93 (<1,000)
A	93-186 (1,000-2,000)
B	186-464 (2,000-5,000)
C	464-4,640 (5,000-50,000)
D	4,640-∞ (50,000-∞)

CUSTOMER KEY:

AM	- Amateur
AR	- Aerial
COM	- Commercial
GOV	- Government
MIL	- Military
MOV	- Movie
PTS	- Portrait Studio
PRO	- Professional
SCH	- School
X-R	- Industrial X-Ray

V-4
114

TABLE V-1
(continued)

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
1232	SCH	7221	C	10	1.3	0	90	0
1421	COM	7333	<A	50	18	10	40	0
1465	AM	7395	C	6	11	3	91	0
1635	AM	7395	C	0	15	1	99	0
2146	AM	7395	C	16	33	α	α	0
2387	X-R	7333	<A	100	100	0	0	0
2465	AM	7395	C	23	64	77	0	0
2488	AM	7395	C	0	100	100	0	0
2714	AM	7395	C	0	22	0.4	99.4	0
2892	GOV	7333						
3075	PRO	7395	B	89	7	2	9	0
3437	AM	7395	C	0	29	100	0	0
3455	AM	7395	C	0	95	95	5	0
3630	AM	7395	C	0	15	1	99	0
4228	AM	7395	C	9	98	91	0	0
4229	AER	7333	<A	100	62	0	0	0
4550	AM	7395	C	0	28	28	72	0
4666	AM	7395	C	0	100	100	0	0
4849	MIL	7333	B	14	93	21	3	63 φ
5120	AM	7395	B	0	5	0	100	0

* All percentages are percent of total production
 α Not given and/or cannot be estimated from processes used
 φ Dichromate from movie production

SIZE KEY: Production, sq m/day (sq ft/day)

- <A <93 (<1,000)
- A 93-186 (1,000-2,000)
- B 186-464 (2,000-5,000)
- C 464-4,640 (5,000-50,000)
- D 4,640-∞ (50,000-∞)

CUSTOMER KEY:

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- MOV - Movie
- PTS - Portrait Studio
- PRO - Professional
- SCH - School
- X-R - Industrial X-Ray

115

TABLE V-1
(continued)

Plant Code	Customer Type	SIC	Size	Percent* Black and White Production	Percent Film Production	Percent Ferricyanide Production	Percent Ferric EDTA Production	Percent Dichromate Production
5359	X-R	7333	B	100	73	0	0	0
5552	AM	7395	C	43	100	57	0	0
6174	AM	7395	C	0	11	2	98	0
6208	MOV	7819	D	4	100	4	0	92
6237	AM	7395	D	3	26	17	80	0
6443	AM	7395	D	α	α	α	α	α
6582	AM	7395	C	0	15	1	99	0
6726	AM	7395	C	8	53	92	0	0
7644	AER	7333	A	80	44	7	13	0
7781	PTS	7221	D	0	2.5	0	100	0
8058	PRO	7395	A	0	8	0	100	0
8226	MOV	7819	C	3	100	15	0	82
9061	MOV	7819	C	1	100	14	0	86
9297	GOV	7333	B	75	53	10	16	0
9942	COM	7333	C	0	40	15	85	0

* All percentages are percent of total production
 α Not given and/or cannot be estimated from processes used

CUSTOMER KEY:

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 MIL - Military
 MOV - Movie
 PTS - Portrait Studio
 PRO - Professional
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 X-R - Industrial X-Ray

SIZE KEY: Production, sq m/day (sq ft/day)

<A <93 (<1,000)
 A 93-186 (1,000-2,000)
 B 186-464 (2,000-5,000)
 C 464-4,640 (5,000-50,000)
 D 4,640-∞ (50,000-∞)

116

taken at 9026; only grab samples were taken from two silver recovery units. The waste stream samples at plant 2714 were collected in 38,000 liter (10,000 gal) tanks prior to discharge. Grab samples were taken from these tanks when they were essentially full.

Plants 4550, 6237 and 1465 were sampled by EPA in the fall of 1974. Plant 4550 was re-sampled in 1977 and the more current data are included in this report. Plant 6237 discharged treated wash water directly to surface waters and concentrated chemicals to a POTW at the time of sampling. Since that time, the plant has combined the waste streams and is discharging to a POTW without end-of-pipe treatment. The data are no longer representative of the plant's operation. Plant 1465 also separates the wash water from the concentrated chemical wastes. The wash water, mixed with some non-contact cooling water, is discharged directly to surface waters without treatment. The concentrated chemicals waste stream is treated and discharged to a POTW. The data for these two streams have been combined and appear later in this section under Effluent Characteristics After End-of-Pipe Treatments.

Plants 6443 and 2488 were sampled by EPA in September 1976. Samples were split with each plant, and the reported pollutant concentrations are averages of the results obtained by the plant and EPA with a few exceptions. The silver value obtained by plant 2488 is reported and the cyanide value obtained by EPA at 6443 is reported. These individual results are more consistent with historical data from similar plants. Both plants use silver recovery and bleach regeneration on all applicable solutions. Plant 2488 treats fix waste by precipitation with ferrous sulfate in a batch operation for cyanide reduction before discharge. No batches were treated and discharged during the sampling period so that the sample taken includes no fix waste except for that carried over into the wash water. Such fix waste is included in the EPA sample from plant 4550. This plant is similar in process and waste handling characteristics to plant 2488. The data for plant 4550 effluent containing the waste fix also appear later in this section.

The samples collected during the 1977 EPA sampling efforts were split with NAPM. The pollutant parameter concentration values reported in the following data tables are an average

of the EPA and NAPM values with the exception of certain parameters measured in the concentrated process solutions (before in-process controls). Because of the concentrated chemical content of these solutions, various chemical interferences caused some inconsistencies in the results between the two labs. The NAPM values for total cyanide and silver were, in general, used for the concentrated solutions. These selections were necessary because it was found that the standard EPA procedures did not consistently give reasonable results for those concentrated chemical solutions. NAPM used modified or other standard test procedures in these cases based on their experience with photographic solutions and obtained results more consistent with the known solution formulations. The following is a brief description of the major modifications made by NAPM on the test procedures.

Total cyanide - In the presence of reducing agents such as sulfites and thiosulfates, an excess of chloramine T is required. After distillation, a determination was made of the amount of reducing agent present. The amount of chloramine T added depended on this result. The EPA procedure calls for a fixed amount.

Silver - On concentrated samples NAPM used long digestion periods of 0.5 to 3 hours with one hour typical. Nitric-sulfuric acid was added during digestion to prevent dryness. EPA digested directly to dryness in considerably less time, potentially resulting in incomplete digestion and low values.

NAPM conducted their own sampling effort in the spring of 1976. The results include 31 plants sampled for two days in 1976 and 6 plants sampled at various times during the period 1973-1976. Each sample is a flow proportioned composite taken from the plant discharge during the daily production period. In some cases the tested samples contain sanitary wastewater. None of these plants use end-of-pipe treatment prior to discharge except plants 32 through 37 which treat waste fix for removal of ferri/ferrocyanide before discharge; however, no treated waste fix was discharged during sampling.

In this section, all production related parameters are expressed in terms of surface area of photographic emulsion

processed in units of thousand square meters with
corresponding English units of thousand square feet in
parentheses.

PROCESSES USED

The processes used by the plants studied are listed in Table V-2. Details of the listed processes were discussed in Section III. In general, the process chemistry and procedure at each plant were the same as that previously described. The variances observed were minor, usually involving wash steps. The number and placement of some wash steps are somewhat dependent upon the type of process machine and squeegee usage. In black and white processing it was common for the stop step to be eliminated. Sometimes a hypo eliminator or hypo clearing agent step was added after fix. Because of the more complicated chemical reactions and critical controls necessary for color processing, there is very little latitude for process variance. Although it is possible to substitute ferricyanide bleach for the prescribed EDTA bleach in the C-41 process, no plants studied made this change. Plant 1232 uses EP-3 chemistry for color paper processing but has eliminated the stabilization step. The process, then, is essentially identical to EP-2 which has no stabilizer step. Plant 3075 uses a bleach-fix in the C-41 and C-22 processes for which separate bleach and fix solutions are prescribed, the bleaches being EDTA and ferricyanide, respectively. This substitution is unusual but both processes had very limited usage.

A list of the plant in-process controls used by plants studied is given in Table V-3. The silver recovery usage column refers to waste fix where "all" means that silver is recovered from each fix solution from each process line. In the primary silver recovery column, the notation "B In-line" refers to a circulating fix solution system where an "in-line" electrolytic silver recovery unit continuously recovers silver from the fix.

Plants 6208 and 7781 recover silver from the after-fix wash waters and recycle a portion of the de-silvered water to process use. Plant 6208 uses an ion exchange system to recover silver from a mixture of waste fix and wash water. A portion of the treated water is chlorinated and recycled

TABLE V-2
PHOTOGRAPHIC PROCESSES USED AT PLANTS STUDIED

PROCESS	PLANTS	0021	0045	0118	0662	1232	1421	1465	1635	2146	2387	2465	2488	2714	2892	3075	3437	3455	3630	4228
Black and White Negative																				
Film			X			1	(1)	1		X	3	X			1	1(1)				X
Paper			X			3	1(1)	2		X					1	1(3)				
Color Negative Film																				
C-22		X			X		1	1	X	X		X		1		(1)	X		X	
C-41		X		X	X	1	(1)	3	X			X		3		1			X	
MC-42												X					X			
ECP-1												X								
ECN-1												X								
ECN-2												X								
MN-31			X																	
Color Negative Paper																				
EP-2		X			X	2	1		X			X		4			X		X	X
EP-3			X	X				3		X										
MC-111																1				
85/86																				
Color Reversal Film (IC)																				
E-3				X			1													
E-4								1		X		X	X				X	2		X
ME-4												X	X							X
EM-25								1				X	X				X	2		X
E-7M												X	X				X			
EA-5															1					
CR1																				
EOO-3												X								X
E-2																1(2)				
Color Reversal Paper (IC)																				
EPR-5										X									1	
Type A								1												
Cibachrome															1					
Color Reversal Film (DC)												X	X							X
K-12																	X	3		
K-14										X		X	X				X	3		X

NOTE: "X" represents presence of machine process lines, and numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses () represent manual process lines. Not all listed process lines are necessarily in operation every day.

V-10
120

TABLE V-2
(continued)

PROCESS	4229	4550	4666	4849	5120	5359	5552	6174	6208	6237	6443	6582	6726	7644	7781	8058	8226	9061	9297	9942
PLANTS																				
Black and White Negative																				
Film	(1)			4		1	X		3	1	X		X	3			X*	1	3	
Paper	1			1		1				1	X			1						
Color Negative Film																				
C-22				(1)				2		1	X	X	X							
C-41		1			X			2		3	X	X		1		1				X
MC-42		1					X					X								
ECP-1				2					8								X	3		
MN-31																		2		
ECN-2									2						1				2	
Color Negative Paper																				
EP-2		2						4		1		X	X	1		2				
EP-3				1							X									X
MC-111																				
85/86					X					3					4					
Color Reversal Film (IC)																				
E-3				(1)																
E-4		1	X	1			X			1			X							X
ME-4			X	1			X													
DN-25		1	X				X			1			X				X			
E-7M		1	X								X		X							
EA-5																				2
CRI									1									1		
EOD-3				1			X													
E-2																				
Color Reversal Paper (IC)																				
EPR-5		1									X		X							1
Type A																				
Cibachrome														1						
Color Reversal Film (DC)							X													
K-12													X							X
K-14		3	X				X			2			X							X

VH
121

NOTE: "X" represents presence of machine process lines, and numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses () represent manual process lines. Not all listed process lines are necessarily in operation every day.
* Includes black and white reversal film.

TABLE V-2
(continued)

PROCESS	PLANTIS	0201	0202	0203	0204	0205	0206	0207	0208	0209	0210	0211	0212	0213	0214	0215	0216	0217	0218	0219	0220
Black & White Negative	Film		1	1	1					1				1		1	1		1	1	
	Paper			1					1					1		1			1	1	1
Color Negative Film	C-22	1			1					1						1		2	2	3	
	C-41		2	2	2		2	1	3	2		2		2	1	2	1	3	2	3	1
	MC-42																				
	ECP-1					1															
	ECI-1																				
	EON-2																				
Color Negative Paper	EP-2									2											
	EP-3	1	1	1	1		3	1	5		3	2	1	2	1	1		5	1	4	1
	MC 111																				
	85/86																				
	Color Reversal Film (IC)																				
Color Reversal Paper (IC)	E-3																				
	E-4																				
	ME-4					1								1							
	EM-25									1											
	E-7M																				
	EA-5																				
	CR1																				
	ECO-3																				
	VNF																				
	Color Reversal Paper (DC)																				
Color Reversal Film (DC)	EPR-5																				
	Type A																				
	Cibachrome																				
	K-12																				
K-14																					

~~V-12~~
122

NOTE: Numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses () represent manual process lines. Not all listed process lines are necessarily in operation every day.

TABLE V-2
(continued)

PROCESS	PLANTS	0221	0222	0223	0224	0225	0226	0227	0228	0229	0230	0231	0232	0233	0234	0235	0236	0237	
Black & White Negative	Film					1		1		1	1								
	Paper					1				1	1								
Color Negative Film	C-22		1	1						2	1	1							
	C-41		3	2	1	2	1			2	1	1	2	2					
	MC-42																		
	FCP-1							1	2			2		1	1				
	P-124	1																	
	MN-31													2	1				
	EGN-2							2					1		1				
Color Negative Paper	EP-2																		
	EP-3			2															
	MC 111		3		1	2	3			1	2								
	85/86																		
Color Reversal Film (IC)	E-3																		
	E-4																		
	ME-4									1			2	2	2	2	1	2	
	EN-25								1				1	2	2	2	2	1	
	E-7M												1	1	1	1	1	1	
	P-112																		
	CRU														1				
	EOD-3																		
	Color Reversal Paper (IC)	EPR-5																	
		Type A					2												
Color Reversal Film (DC)	K-12																		
	K-14												3	4	3	3	3	3	
	RCP-2												2	2	3	1	2	2	
															1	2	2	1	

NOTE: Numbers represent number of machine process lines of each plant. Some machines are capable of processing multiple strands. Numbers in parentheses () represent manual process lines. Not all listed process lines are necessarily in operation every day.

V-13
123

TABLE V-3
RECOVERY AND REGENERATION AT PLANTS STUDIED

Plant Code	SILVER RECOVERY				BLEACH REGENERATION						DEVELOPER		WASH WATER SILVER RECOVERY Method
	Usage	METHODS			Usage	Ferri-cyanide	EDTA	Chromate	Alcarch-Fix	Coupler Recovery	Regener-ation		
		Primary	Tailing	Usage									
0021	All	A, B	A	All	D	G	NA	F	NA	X	None		
0045	All	A	None	All	NA	F	NA	F	NA	X	None		
0118	All	A	None	Partial	X	F	NA	F	NA	X	None		
0662	All	A, B	A	All	D	G	NA	F	NA	X	None		
1232	All	A	None	All	NA	F	NA	F	NA	X	None		
1421	All	A, Y	None	Partial	X	F	NA	F	NA	X	None		
1465	All	A, B	A, B	Partial	X, E	G	NA	F	NA	X	None		
1635	All	A, B	A	All	D	G	NA	F	NA	X	None		
2146	All	A, B	NG	All	D	F	NA	F	NA	X	None		
2387	All	B In-Line	B	NA							None		
2465	All	A, B	B	All	D	NA	NA	NA	NA	X	None		
2488	All	A, B	B	All	D	NA	NA	NA	NA	X	None		
2714	All	A, B	A	All	D	G	NA	F	NA	X	None		
2892	Partial	A, B, B In-Line	B	Partial	B	NA	NA	NA	NA	X	None		
3075	Partial	A, B, Y	None	None	X	X	NA	X	NA	X	None		
3437	All	A, B	B	All	D	NA	NA	NA	NA	X	None		
3455	All	A, B In-Line	B	All	E	NA	NA	F	NA	X	None		
3630	All	A, B	A	All	D	G	NA	F	NA	X	None		
4228	All	A, B	B	All	D	NA	NA	NA	NA	X	None		

KEY:
A - Metallic Replacement
B - Electrolytic
C - Resin Ion Exchange
D - Persulfate
E - Ozone
F - Aeration and Chemical Addition
G - Chemical Addition
H - Acidify with Sodium Disulfate
I - Acidify with Carbon Dioxide
J - Reverse Osmosis
K - Precipitation and Settling
NA - Not Applicable
X - Used and Not Regenerated
Y - Off-Site Recovery
NG - Not Given

~~V-14~~
124

TABLE V-3
(continued)

Plant Code	SILVER RECOVERY			BLEACH REGENERATION					DEVELOPER		WASH WATER SILVER RECOVERY	
	METHODS			METHODS					Coupler Recovery	Regeneration	Method	
	Usage	Primary	Tailing	Usage	Ferri-cyanide	EDTA	Chromate	Bleach-Fix				
4229	All	B	B	NA						NA	X	None
4550	All	A,B	B	All	D	F	NA	F		H	X	None
4666	All	A,B	B	All	D	NA	NA	NA		H	X	None
4849	All	A,B	None	Partial	X,D	NA	G	F		NA	G	None
5120	All	A,B	NG	All	NA	F	NA	F		NA	X	None
5359	All	B	A	NA						NA	X	None
5552	All	A,B	B	All	D	NA	NA	NA		H	X	None
6174	All	A,B	A	All	D	G	NA	F		NA	X	None
6208	All	B,B In-Line	B,C	Partial	D	NA	X	NA		NA	G	C
6237	All	A,B	None	Partial	X,D	G	NA	X,F		I	X	None
6443	All	A,B	B	All	D	F	NA	F		NA	X	None
6582	All	A,B	A	All	D	G	NA	F		NA	X	None
6726	All	A,B	B	All	D	NA	NA	NA		H	X	None
7644	Partial	B	None	None	NA	X	NA	X		NA	X	None
7781	All	B	A	All	NA	G	NA	F		NA	X	J,K
8058	All	A	None	All	NA	G	NA	F		NA	X	None
8226	All	A	None	All	D	NA	G	NA		NA	X	None
9061	All	B,B In-Line	B	All	D	NA	G	NA		NA	X	C
9297	All	B,B In-Line	B	All	E	NA	NA	F		NA	X	None
9942	All	A	None	Partial	X	F	NA	F		NA	X	None

KEY:
A - Metallic Replacement
B - Electrolytic
C - Resin Ion Exchange
D - Persulfate
E - Ozone
F - Aeration and Chemical Addition
G - Chemical Addition
H - Acidify with Sodium Bisulfate
I - Acidify with Carbon Dioxide
J - Reverse Osmosis
K - Precipitation and Settling
NA - Not Applicable
X - Used and Not Regenerated
Y - Off-Site Recovery
NG - Not Given

V-15
125

TABLE V-3
(continued)

Plant	Use of Silver Recovery on Fix Solutions		Regeneration of Bleaches	
	Usage	Method	Ferricyanide Bleach	Other Bleaches
0201	All	A	No	Yes
0202	All	A,B	NA	Yes
0203	All	B	NA	Yes
0204	Partial	A	No	Partial
0205	Partial	B	No	NG
0206	All,NIS	A,B	NA	Yes
0207	All	A	NA	Yes
0208	All	A	Yes	Yes
0209	Partial	A	NA	Partial
0210	All	A	No	Yes
0211	All	A,B	NA	Yes
0212	All	A	NA	No
0213	All	B	No,NIS	Yes
0214	All	A	NA	NG
0215	All	A	Yes	Yes
0216	All	A	NA	No,NIS
0217	All	A,B	Partial	Yes
0218	Partial	A,B	No	Yes
0219	All	A	No,NIS	Yes
0220	All	A	NA	Yes
0221	All	B	NA	No
0222	All	A	No	Yes
0223	Partial	A,B	Yes	Partial
0224	All	A	NA	Yes
0225	All	A	NA	Yes
0226	All	A,B	NA	No
0227	Partial	B	Partial	Yes
0228	Partial	B	Partial	Yes
0229	Partial	C	No	No
0230	Partial	A	No,NIS	NG
0231	All	B	Partial	Partial
0232-0237	All,NIS	B	Yes	No
				Yes

KEY: A - Metallic Replacement
 B - Electrolytic
 C - Off-site
 NA - Not Applicable
 NG - Information Not Given
 NIS - Waste Not Included in Sample

~~V-16~~
126

to the process. The waste fix has gone through primary and tailing silver recovery prior to mixing with the wash water. The silver is recovered from the resin on site by backwashing the resin with a proprietary concentrate. Plant 7781 treats the wash water with a reverse osmosis (RO) system and removes the silver from the concentrate by sulfide precipitation and settling. Before introduction to the RO unit, the wash water is equalized and filtered. Plant 9061 also uses a proprietary resin ion exchange system to recover silver from wash water. The silver is recovered from the resin off site by a contractor and the waste wash water is discharged.

While ferricyanide and ferric EDTA bleach regeneration is not as universally practiced as silver recovery at the plants visited, most plants do some regeneration of bleach. In most cases where a bleach was not regenerated, it was from a little-used process.

Dichromate bleach is not regenerated. Some plants reuse a portion of the bleach overflow by discharging a portion and reconstituting the remainder. Plant 6208 uses a "replenish-on-demand" dichromate bleach replenishment technique which was described in Section III. In addition the plant uses a resin ion exchange system to reduce the chromium level in the after bleach wash water prior to recycle of the water.

WATER USE

Water is used in the photographic processing industry for the following purposes:

- (1) Process water: film and paper wash water, solution make-up water, and area and equipment wash water.
- (2) Non-process water: Non-contact cooling and heating water, cooling tower (air conditioning), boiler, and sanitary.

The total (process and non-process) water use for the facilities visited in the industry ranges from 13,200 to 2,100,000 liters per day (3,500 to 550,000 gallons per day). It was observed that more than 95 percent of the process

water use in each facility is for film and paper washing. Unless otherwise stated, water use throughout this document refers to process water only.

Process Water

Film and Paper Wash Water

The largest single water process use is for the washing of film and paper during various stages of the process. The function of the wash step is to remove no longer needed chemicals included in the emulsion during manufacture, absorbed into the emulsion during processing, or reaction products created during processing.

Solution Make-up Water

The chemicals used to make up processing solutions are generally supplied to the processor in the form of liquid concentrates or powdered chemical formulations. The processor adds water to make up the solutions to working strength. Waterborne wastes are generated when these solutions are discarded after becoming exhausted or when allowed to overflow during replenishment, as is the common practice.

Area and Equipment Wash Water

Water is used for the washing and rinsing of solution mixing utensils, storage tanks, and processing machines and for area washdown.

Non-Process Water

Some facilities use non-contact water for the heating and cooling of process solutions to maintain proper operating temperatures. This water is not process water since it is contained in enclosed water jackets around process tanks and does not come into contact with raw materials or the product. Other non-process water uses include make-up water for cooling towers, boilers, and lawn sprinkling. The volume of water used for these purposes in this industry is small when compared to process water use except in the case of large plants with cooling towers for air conditioning.

Water Usage

Some general information on water use is included in the results of the industry survey and the EPA telephone survey tabulated in Section III. This information is in terms of ranges of total process water use. During the EPA plant visits, estimates of detailed water use information were obtained from the 20 plants visited, and these estimates are presented in Table V-4 along with total process water use for the remainder of the plants studied. The average total process water use for the 70 plants from which data were obtained is 157,000 liters/1,000 sq m (3,850 gal/1,000 sq ft) of material processed.

PROCESS WASTE

Process waste information was obtained from EPA sampling in 1974, 1976 and 1977, the NAPM sampling effort, and plant supplied self-monitoring data. A major portion of the 1977 EPA sampling effort was devoted to the sampling and analyses for toxic pollutants at four of the five plants sampled. Most of the data were obtained from wastewater samples taken after the application of various controls. The 1977 EPA sampling effort also included the sampling of some process solutions before application of controls. These data were obtained to assist in evaluating the effectiveness of various controls. The production normalizing factor used to calculate the cyanide and chromium amounts found in the following tables relates to the area of emulsion processed using ferricyanide bleach or chromium bleach, respectively. In reference to the cyanide values obtained during the NAPM survey, the actual parameter measured was ferri/ferrocyanide. The listed total cyanide value was calculated by NAPM by multiplying the measured value by the stoichiometric ratio of 0.74.

Tables V-5 and V-6 contain pollutant concentration and quantity information, respectively, on various process solutions before any application of controls. These data were obtained from grab samples collected by EPA during the 1977 sampling effort. The solutions selected for sampling were those solutions that the particular plant reconstituted or regenerated for reuse. With these data, estimates can be made as to the impact on an effluent of not reusing these solutions.

~~V-19~~
129

TABLE V-4
ESTIMATED WATER USE FOR PLANTS IN THE PHOTOPROCESSING INDUSTRY

Plant Code	Water Intake liters/1,000 sq m (gal/1,000 sq ft)	Solution Make-up liters/1,000 sq m (gal/1,000 sq ft)	Film and Paper Wash liters/1,000 sq m (gal/1,000 sq ft)	Area Wash Down liters/1,000 sq m (gal/1,000 sq ft)	Total Process liters/1,000 sq m (gal/1,000 sq ft)
0021	*	**	**	**	64,000 (1,600)
0045	*	**	**	**	288,000 (7,060)
0118	*	*	*	*	*
0662	*	**	**	**	80,000 (2,000)
1232	84,700 (2,080)	200 (5.0)	82,700 (2,030)	200 (5.0)	83,100 (2,040)
1421	1,670,000 (41,000)	5,700 (140)	505,000 (12,400)	2,200 (55)	513,000 (12,600)
1465	289,000 (7,100)	4,000 (99)	153,000 (3,760)	*	157,000 (3,860)
1635	*	**	**	**	78,000 (1,900)
2146	*	**	**	**	160,000 (3,900)
2387	*	1,000 (25)	101,000 (2,470)	negligible	101,000 (2,490)
2465	*	**	**	**	192,000 (4,700)
2488	*	**	**	**	96,000 (2,400)
2714	21,000 (520)	570 (14)	18,300 (450)	190 (4.6)	19,200 (470)
2892	538,000 (13,200)	**	**	**	**
3075	167,000 (4,100)	530 (13)	161,000 (3,950)	200 (5)	162,000 (3,970)
3437	*	**	**	**	110,000 (2,700)
3455	448,000 (11,000)	7,130 (175)	361,000 (8,870)	3,800 (93)	372,000 (9,140)
3630	*	**	**	**	73,000 (1,800)
4228	*	**	**	**	270,000 (6,600)

* Not given

** Not allocated

131
0-20

TABLE V-4
(continued)

Plant Code	Water Intake liters/1,000 sq m (gal/1,000 sq ft)	Solution Make-up liters/1,000 sq m (gal/1,000 sq ft)	Film and Paper Wash liters/1,000 sq m (gal/1,000 sq ft)	Area Wash Down liters/1,000 sq m (gal/1,000 sq ft)	Total Process liters/1,000 sq m (gal/1,000 sq ft)
4229	192,000 (4,700)	**	**	**	143,000 (3,500)
4550	407,000 (10,000)	4,100 (100)	102,000 (2,500)	*	106,000 (~2,600)
4666	*	**	**	**	207,000 (5,100)
4849	570,000 (14,000)	61,000 (1,500)	497,000 (12,200)	9,400 (230)	570,000 (14,000)
5120	*	**	**	**	57,000 (1,400)
5359	149,000 (3,650)	450 (11)	146,000 (3,580)	94 (2.3)	147,000 (3,600)
5552	*	**	**	**	109,000 (2,700)
6174	*	*	*	*	49,500 (1,200)
6208	103,000 (2,520)	1,400 (34)	98,000 (2,410)	340 (8.4)	100,000 (2,450)
6237	*	1,400 (35)	40,300 (990)	1,400 (35)	43,200 (1,060)
6443	53,800 (1,320)	**	**	**	51,300 (1,260)
6582	*	**	**	**	92,000 (2,300)
6726	*	**	**	**	200,000 (4,900)
7644	135,000 (3,300)	780 (19)	120,000 (2,950)	1,960 (48)	122,000 (3,000)
7781	17,500 (430)	490 (12)	3,600 (89)	4,900 (120)	9,000 (220)
8058	171,000 (4,200)	1,800 (45)	36,300 (890)	negligible	38,300 (940)
8226	*	**	**	**	180,000 (4,400)
9061	619,000 (15,200)	220 (5.5)	530,000 (13,000)	*	530,000 (13,000)
9297	522,000 (12,800)	10,600 (260)	281,000 (6,900)	*	293,000 (~7,200)
9942	*	*	*	*	*

* Not given

** Not allocated

TABLE V-4
(continued)

Plant Code	Total Process Water		Plant Code	Total Process Water	
	1/1,000 sq m (gal/1,000 sq ft)	(gal/1,000 sq ft)		1/1,000 sq m (gal/1,000 sq ft)	(gal/1,000 sq ft)
0201	188,000	(4,610)	0220	167,000	(4,090)
0202	171,000	(4,200)	0221	63,200	(1,550)
0203	291,000	(7,140)	0222	155,000	(3,800)
0204	111,000	(2,720)	0223	28,600	(700)
0205	258,000	(6,340)	0224	62,000	(1,520)
0206	165,000	(4,050)	0225	137,000	(3,360)
0207	46,400	(1,140)	0226	106,000	(2,600)
0208	105,000	(2,580)	0227	259,000	(6,350)
0209	288,000	(7,060)	0228	28,100	(690)
0210	110,000	(2,710)	0229	NA	
0211	51,900	(1,270)	0230	108,000	(2,650)
0212	3,280,000	(80,500)*	0231	83,800	(2,060)
0213	109,000	(2,670)	0232	280,000	(6,880)
0214	137,000	(3,370)	0233	193,000	(4,740)
0215	205,000	(5,040)	0234	419,000	(10,300)
0216	13,900,000	(342,000)*	0235	201,000	(4,940)
0217	44,800	(1,100)	0236	141,000	(3,460)
0218	96,800	(2,380)	0237	252,000	(6,180)
0219	50,600	(1,240)			

* Not included in overall average. Plants indicated values not representative of normal water use.

NA Total water intake not allocated to process water and non-process use.

TABLE V-4
(continued)

Plant Code	Sanitary liters/1,000 sq m (gal/1,000 sq ft)	Non-Contact Heating and Cooling liters/1,000 sq m (gal/1,000 sq ft)	Other Non-Process liters/1,000 sq m (gal/1,000 sq ft)	Total Non-Process liters/1,000 sq m (gal/1,000 sq ft)
0021	*	*	*	*
0045	*	*	*	*
0118	*	*	*	*
0662	*	*	*	*
1232	1,800 (45)	None	None	1,800 (45)
1421	334,000 (8,200)	672,000 (16,500)	*	*
1465	3,000 (74)	None	129,000 (3,170)	132,000 (3,240)
1635	*	*	*	*
2146	*	*	*	*
2387	2,500 (62)	None	*	*
2465	*	*	*	*
2488	*	*	*	*
2714	2,200 (55)	None	None	2,200 (55)
2892	*	*	*	*
3075	5,300 (130)	None	None	5,300 (130)
3437	*	*	*	*
3455	7,130 (175)	67,600 (1,660)	*	*
3630	*	*	*	*
4228	*	*	*	*

* Not given
** Not allocated

V-23
133

TABLE V-4
(continued)

Plant Code	Sanitary Liters/1,000 sq m (gal/1,000 sq ft)	Non-Contact Heating and Cooling Liters/1,000 sq m (gal/1,000 sq ft)	Other Non-Process Liters/1,000 sq m (gal/1,000 sq ft)	Total Non-Process Liters/1,000 sq m (gal/1,000 sq ft)
4229	49,000 (1,200)	None	None	48,900 (1,200)
4550	8,600 (210)	85,600 (2,100)	25,300 (620)	118,000 (2,900)
4666	*	*	*	*
4849	*	*	*	*
5120	*	*	*	*
5359	1,700 (42)	None	450 (11)	2,200 (53)
5552	*	*	*	*
6174	*	*	*	*
6208	2,000 (50)	None	700 (17)	2,700 (67)
6237	*	*	*	*
6443	*	*	*	*
6582	*	*	*	*
6726	*	*	*	*
7644	13,800 (340)	None	None	13,800 (340)
7781	4,500 (110)	3,600 (89)	130 (3.2)	8,100 (200)
8058	14,700 (360)	None	120,000 (2,950)	134,000 (3,300)
8226	*	*	*	*
9061	4,500 (110)	84,700 (2,080)	220 (5.5)	89,200 (2,190)
9297	**	**	**	288,000 (5,600)
9942	*	*	*	*

* Not given

** Not allocated

V-24
134

Table V-7 contains data obtained from grab samples taken before and after various silver recovery operations. These samples were taken during the 1977 EPA sampling effort.

Tables V-8 and V-9 contain pollutant concentration and quantity information, respectively, on the effluent from plants using in-process controls for silver recovery, coupler recovery, and bleach regeneration where applicable. A description of the in-process controls used at the plants was previously given in Table V-3. The hydraulic load values given in Table V-9 may not always agree with the process water values for a specific plant given in Table V-4. The process water information in Table V-4 represents estimates or long-term averages in most cases while the water data in Table V-9 generally represent a measured flow over a relatively short sampling period.

EFFLUENT CHARACTERISTICS

The results in this section describe plant effluents after the application of various end-of-pipe treatments. These treatments are in addition to the various controls which were previously described.

End-of-pipe treatment information for plants using such treatments is given in Table V-10. Table V-11 contains before- and after-treatment data for some individual treatment operations. Tables V-12 and V-13 contain the plant effluent data for plants using in-process controls plus end-of-pipe treatments, pollutant concentrations, and amounts, respectively.

TABLE V-6
 PROCESSING MACHINE TANK OVERFLOW COMPOSITION WITHOUT APPLICATION OF IN-PROCESS CONTROLS - POLLUTANT AMOUNT

Plant Code	Stream Description	Hydraulic Load, liters/sq m (gal/1,000 sq ft)	Pollutant Quantity, kg/1,000 sq m (lb/1,000 sq ft)			
			Cyanide	Cadmium	Chromium	Silver
2714	Ferricyanide Bleach	2,800 (69)	44 (9.1)	<5.6 x 10 ⁻⁵ (<1.1 x 10 ⁻⁵)	1.2 x 10 ⁻² (2.4 x 10 ⁻³)	1.15 x 10 ⁻² (2.35 x 10 ⁻³)
	EDTA Bleach	570 (14)	--	<1.1 x 10 ⁻⁵ (<2.3 x 10 ⁻⁶)	1.1 x 10 ⁻³ (2.3 x 10 ⁻⁴)	0.15 (0.03)
	Bleach-Fix	290 (7.1)	--	<5.8 x 10 ⁻⁶ (<1.2 x 10 ⁻⁶)	1.7 x 10 ⁻⁴ (3.6 x 10 ⁻⁵)	0.61 (0.12)
4550	Ferricyanide Bleach	810 (20)	40.9 (8.38)	3.3 x 10 ⁻⁴ (6.7 x 10 ⁻⁵)	1.5 x 10 ⁻³ (2.2 x 10 ⁻⁴)	6.5 x 10 ⁻³ (1.3 x 10 ⁻¹)
	EDTA Bleach	1,700 (42)	0.0054 (0.0011)	6.8 x 10 ⁻⁴ (1.4 x 10 ⁻⁴)	2.0 x 10 ⁻² (4.2 x 10 ⁻³)	0.40 (0.08)
	Bleach-Fix (R-5)	610 (15)	4.3 x 10 ⁻⁴ (8.8 x 10 ⁻⁵)	<3.7 x 10 ⁻⁴ (<7.5 x 10 ⁻⁵)	3.5 x 10 ⁻³ (7.1 x 10 ⁻⁴)	1.24 (0.25)
	Bleach-Fix (EP-2)	320 (7.9)	3.5 x 10 ⁻⁴ (7.2 x 10 ⁻⁵)	3.7 x 10 ⁻⁴ (6.6 x 10 ⁻⁵)	1.9 x 10 ⁻³ (3.9 x 10 ⁻⁴)	0.51 (0.10)
	Color Developer	660 (16.2)	--	2.24 x 10 ⁻⁴ (4.59 x 10 ⁻⁵)	6.0 x 10 ⁻⁵ (1.2 x 10 ⁻⁵)	9.2 x 10 ⁻⁴ (1.9 x 10 ⁻⁴)
6208	Ferricyanide Bleach	190 (4.75)	2.9 (0.59)	<3.8 x 10 ⁻⁶ (<7.8 x 10 ⁻⁷)	1.7 x 10 ⁻⁵ (3.6 x 10 ⁻⁶)	7.2 x 10 ⁻⁵ (1.5 x 10 ⁻⁵)
	Dichromate Bleach	120 (2.86)	--	7.9 x 10 ⁻⁵ (1.6 x 10 ⁻⁵)	0.26 (0.05)	7.8 x 10 ⁻⁵ (1.6 x 10 ⁻⁵)
7781	Color Developer	200 (5.0)	--	1.7 x 10 ⁻² (3.5 x 10 ⁻³)	2.0 x 10 ⁻⁵ (4.1 x 10 ⁻⁶)	3.0 x 10 ⁻⁴ (6.1 x 10 ⁻⁵)
	Color Developer	330 (8.0)	--	3.6 x 10 ⁻⁴ (7.3 x 10 ⁻⁵)	8.6 x 10 ⁻⁵ (1.8 x 10 ⁻⁵)	1.6 x 10 ⁻⁴ (3.3 x 10 ⁻⁵)
	EDTA Bleach	210 (5.1)	--	1.9 x 10 ⁻⁵ (3.9 x 10 ⁻⁶)	7.6 x 10 ⁻⁴ (1.6 x 10 ⁻⁴)	7.6 x 10 ⁻⁷ (1.6 x 10 ⁻²)
	Bleach-Fix	310 (7.7)	--	2.5 x 10 ⁻² (5.1 x 10 ⁻³)	4.0 x 10 ⁻⁴ (8.2 x 10 ⁻⁵)	1.35 (0.28)
	Bleach-Fix	330 (8.0)	--	7.9 x 10 ⁻⁵ (1.6 x 10 ⁻⁵)	9.6 x 10 ⁻⁴ (2.0 x 10 ⁻⁴)	0.70 (0.14)

V-27
 137

TABLE V-6
(continued)

Plant Code	Stream Description	Pollutant Quantity, kg/1,000 sq m (lb/1,000 sq ft)							
		DOC	BOD	Nitrogen ^{am}	Ammonia	Iron	Lead	TSS	TDS
2714	Ferricyanide Bleach	37 (7.5)	--	--	--	15.6 (3.2)	6.2 x 10 ⁻⁴ (1.3 x 10 ⁻⁴)	0.083 (0.017)	360 (74)
	EDTA Bleach	25 (5.1)	--	--	--	9.2 (1.9)	<1.1 x 10 ⁻⁵ (~2.3 x 10 ⁻⁶)	0.035 (0.0072)	150 (30)
	Bleach-Fix	13 (2.7)	--	--	--	1.4 (0.3)	1.5 x 10 ⁻⁴ (3.0 x 10 ⁻⁵)	0.032 (0.0066)	59 (12)
	Ferricyanide Bleach	25.0 (5.13)	8.2 (1.7)	2.5 (0.52)	9.0 (1.8)	1.6 (0.3)	0.083 (0.017)	0.083 (0.017)	250 (51)
	EDTA Bleach	72.3 (14.8)	14.2 (2.91)	110 (22)	20.6 (4.2)	3.4 x 10 ⁻³ (7.0 x 10 ⁻⁴)	0.19 (0.039)	0.19 (0.039)	390 (80)
4550	Bleach-Fix (R-5)	20.7 (4.24)	8.11 (1.66)	23 (4.8)	4.7 (0.96)	6.1 x 10 ⁻⁴ (1.2 x 10 ⁻⁴)	0.034 (0.0070)	0.034 (0.0070)	120 (24)
	Bleach-Fix (EP-2)	15.2 (3.11)	9.01 (1.85)	9.8 (2.0)	2.6 (0.5)	4.5 x 10 ⁻⁴ (9.2 x 10 ⁻⁵)	0.026 (0.0054)	0.026 (0.0054)	68 (14)
	Color Developer	4.26 (0.872)	--	--	--	1.9 x 10 ⁻³ (3.9 x 10 ⁻³)	1.65 x 10 ⁻⁴ (3.38 x 10 ⁻⁵)	0.0064 (0.0013)	27 (5.5)
	Ferricyanide Bleach	1.6 (0.33)	--	--	1.44 (0.29)	8.0 x 10 ⁻⁵ (1.6 x 10 ⁻⁵)	0.0049 (0.0010)	0.0049 (0.0010)	19 (3.9)
	Dichromate Bleach	0.046 (0.0094)	--	--	8.4 x 10 ⁻³ (1.7 x 10 ⁻⁵)	<2.4 x 10 ⁻⁶ (~4.9 x 10 ⁻⁷)	0.0014 (0.00029)	0.0014 (0.00029)	6.8 (1.4)
7781	Color Developer (A)	3.06 (0.626)	--	--	--	4.8 x 10 ⁻⁴ (9.8 x 10 ⁻⁵)	1.5 x 10 ⁻³ (3.1 x 10 ⁻⁴)	3.6 x 10 ⁻¹ (7.5 x 10 ⁻⁴)	16 (3.3)
	Color Developer (B)	5.51 (1.13)	--	--	--	1.2 x 10 ⁻¹ (2.5 x 10 ⁻¹)	3.0 x 10 ⁻⁵ (6.1 x 10 ⁻⁶)	3.3 x 10 ⁻³ (6.7 x 10 ⁻⁴)	17 (3.5)
	EDTA Bleach	4.61 (0.945)	--	--	--	1.6 (0.3)	2.9 x 10 ⁻⁴ (6.0 x 10 ⁻⁵)	0.018 (0.0037)	43 (8.8)
	Bleach-Fix (A)	13.0 (2.67)	--	--	--	1.65 (0.34)	6.8 x 10 ⁻² (1.4 x 10 ⁻²)	0.039 (0.0080)	78 (16)
	Bleach-Fix (B)	16.5 (3.39)	--	--	--	4.4 (0.9)	2.3 x 10 ⁻⁴ (4.7 x 10 ⁻⁵)	0.017 (0.0034)	98 (20)

V-28
138

TABLE V-7
BEFORE AND AFTER RESULTS OF VARIOUS SILVER RECOVERY OPERATIONS

Plant Code	Sampled Stream Description	Control Type	Date	Pollutant Concentration, mg/liter										
				Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Phenols	Iron	Leak	TSS	TDS
4550	Bleach-fix (EP-2) before SR	Silver recovery	7-77	1.1	47,150	1.0	7.0	1,500	28,000	0.04	86,960	1.33	82	209,100
	Bleach-fix (EP-2) after SR	Silver recovery	--	--	--	--	--	4.7	--	--	--	--	--	--
6208	Influent to ion exchange	SR from wash water and recycle	8-77	0.02	29	0.017	0.21	2.0	--	0.15	0.10	0.05	14.1	1,000
	Ion exchange effluent	SR from wash water and recycle	--	0.01	25	0.013	0.10	0.14	--	0.03	0.09	0.05	3.5	973
7781	Influent to RO	Wash water	8-77	--	153	0.017	0.04	68	--	0.73	39	0.19	103	1,210
	RO permeate	recycle	--	--	635	0.25	0.02	14	--	18.3	26	0.08	1	3,060
	RO concentrate (influent to metals removed)	SR and end-of-pipe treatment for reduction of heavy metals	--	--	3,710	4.9	0.72	57	--	11.3	340	1.8	34	26,480
	partial influent to aeration	metals	--	--	3,450	0.06	0.16	0.08	--	4.9	5.8	0.07	19.4	53,100
9061	Influent to ion exchange no. 1	SR from wash water and recycle	8-77	0.32	37	0.013	0.26	0.74	--	0.02	0.92	0.01	10.2	853
	Ion exchange effluent no. 1	water and recycle	--	0.03	<5	0.02	0.02	0.04	--	0.02	0.20	0.05	2.5	586
	Influent to ion exchange no. 2		--	<0.01	21	0.02	0.06	0.60	--	0.02	0.18	0.05	5.5	695
	Ion exchange effluent no. 2		--	<0.01	4.4	0.013	0.04	0.10	--	0.02	0.19	0.05	11.8	690

139

TABLE V-8
EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - CONCENTRATION

Plant Code	Sample Information		Date	By	Pollutant Concentration, mg/liter										
	Description				Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Ammonia-Nitrogen	Iron	Lead	TSS	TDS
0021	Avg. of 3 24-hr. composites ¹		1977	Self	0.18	--	--	--	2.4	507	--	--	--	--	1,002
0045	See Table V-12														
0118	Avg. of 1 to 3 8-hr. FP composites		75-76	Self	4.0	--	<0.01	0.60	0.20	96	--	--	<0.09	14	681
0662	Single 24-hr. composite ¹		4-77	Self	1.09	--	--	--	1.5	497	--	--	--	--	662
1232	Not available														
1330	Avg. of 5 daily FP composites		1-76	Self	0.001	--	0.001	0.005	0.71	--	--	--	0.0009	14	--
1421	Avg. of 10 monthly samples		76-77	Self	--	--	--	--	0.20	30	5.5	2.90	--	8	--
1465	See Table V-12														
1635	Avg. of 3 24-hr. composites ¹		1977	Self	0.30	--	--	--	3.3	326	--	--	--	--	1,184
2146	Single 24-hr. FP composite		12-76	Self	5.6	--	--	<0.005	2.0	245	--	--	--	4	--
2387	Not available														
2465	Single 24-hr. FP composite ⁵		9-76	Self	4.2	--	<0.02	0.07	0.46	300	--	--	<0.02	60	1,860
2488	Single 24-hr. FP composite ⁵		7-76	Self	3.8	--	<0.02	0.23	0.33	240	--	--	0.04	115	1,950
2488	Single 13.5-hr. FP composite ⁵		9-76	EPA	7.5	--	<0.02	0.02	0.37	85	7.05	4.2	--	64	--
2714	See Table V-12														
2892	Not available														
3075	Not available														
3437	Avg. of 2 24-hr. composites ⁵		1976	Self	2.4	--	<0.02	0.07	0.26	229	--	1.3	<0.02	6.4	1,187
3455	Not available														
3630	Avg. of 4 24-hr. composites ⁴		1977	Self	1.1	--	--	--	0.59	76	--	--	--	--	519
4228	Avg. of 2 24-hr. FP composites ⁵		1976	Self	8.0	--	<0.02	0.03	0.50	140	--	3.7	<0.03	48	1,610

1 FP - flow proportioned.
 2 Plant has divided process wastewaters into two or more outfalls. Pollutants summed in proportion to stream flow.
 3 Represents only portion of total plant discharge of process water.
 4 Discharge does not include ferricyanide bleach waste which is contractor hauled.
 5 Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix not in sample.

V-30
140

TABLE V-8
(continued)

Plant Code	Sample Information			Pollutant Concentration, mg/liter										
	Description	Date	By	Cyanide	TVC	Cadmium	Chromium	Silver	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
4229	Not available													
4550	Avg. of 3 24-hr. FT Composites	7-77	EDA	0.4	109	0.01	0.10	0.33	175	9.3	5.9	0.04	25	1,950
4550	Single 24-hr. FT Composite	7-76	Self	0.7	--	<0.02	0.23	0.26	<70	--	23	0.03	15	1,790
4666	Avg. of 4 24-hr. FT Composites	1976	Self	8.1	--	<0.02	0.04	0.33	484	--	4.3	<0.03	29	2,056
4849	Not available													
5120	Single Grab	12-77	Self	0.30 ¹	--	0.007 ³	0.0017	0.023	8 ¹	--	--	--	<0.5 ³	423 ¹
5359	Not available													
5552	Single 24-hr. Composite	8-76	Self	10	--	<0.02	0.07	0.55	165	--	4.2	<0.02	108	1,900
6174	Avg. of 8 24-hr. Composites	76-77	Self	0.67	--	--	--	1.06	506	--	--	--	--	1,086
6208	Avg. of 6 24-hr. FT Composites	1977	Self	0.45	--	--	3.2	0.17	90	--	0.41	--	12	--
6208	Avg. of 3 24-hr. FT Composites	8-77	EDA	0.01	44	0.019	2.8	0.47	78	13	0.19	<0.05	32.4	1,245
6237	Not available													
6443	Single 24-hr. FT Composite	9-76	EDA	0.73	286	<0.02	0.08	3.24	237	69	36.5	--	42	--
6582	Avg. of 3 24-hr. Composites	1977	Self	0.95	--	--	--	1.38	132	--	--	--	--	904
6726	Single 24-hr. Composite	7-76	Self	3.5	--	<0.02	0.08	0.82	165	--	1.52	<0.02	9	780
7644	Not available													
7781	See Table V-12													
8058	Not available													
8226	Single 24-hr. FT Composite	3-76	Self	0.54	--	--	0.75	0.3	209	--	--	--	88	--
9061	Not available													
9297	Not available													
9942	Avg. of 1 to 3 8-hr. FT Composites	75-76	Self	3.99	--	<0.01	<0.01	0.29	28	--	--	<0.02	5.4	369

141

¹ FT - flow proportioned.
² Plant has divided process wastewaters into two or more outfalls. Pollutants summed in proportion to stream flow.
³ Represents only portion of total plant discharge of process water.
⁴ Discharge does not include ferricyanide bleach waste which is contractor hauled.
⁵ Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix not in sample.

TABLE V-8
 EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - CONCENTRATIONS
 (continued)

Plant Code	POLLUTANT CONCENTRATION mg/liter				
	BOD	COD	Ag	Total CN	
0201	156	288	0.77	7.8	
0202	204	516	0.87		
0203	61.2	192	0.89		
0204	228	588	5.0	2.7	
0205	431	876	3.5	53	
0206	180	384	0.48		
0207	336	1,190	16.8		
0208	336	1,920	12.0		
0209	63.5	312	1.8		
0210	168	312	0.77	2.1	
0211	168	480	2.64		
0212	40.7	180	0.25		
0213	132	276	1.9	10.8	
0214	312	576	2.4		
0215	132	408	4.2	0.4	
0216	10.1	34.8	4.5		
0217	395	936	5.8	1.4	
0218	264	876	1.1	3.4	
0219	192	804	2.6	0.8	
0220	98.3	360	2.9		
0221	44.3	288	5.4		
0222	132	480	0.76		

V-32
 142

TABLE V-8
 EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - CONCENTRATIONS
 (continued)

Plant Code	POLLUTANT CONCENTRATION mg/liter			
	BOD	COD	Ag	Total CN
0223	527	288	7.7	0.6
0224	252	624	1.0	
0225	204	576	1.8	
0226	192	552	2.0	
0227	240	444	2.5	1.6
0228	76.7	300	1.7	4.6
0229	55.1	144	1.0	2.1
0230	348	936	7.2	
0231	56.3	276	0.52	
0232	372	708	4.7	4.5
0233	228	636	0.25	3.1
0234	156	312	0.14	6.2
0235	204	1,040	0.94	6.8
0236	75.5	276	0.62	4.2
0237	168	1,200	0.56	5.4

V-33
 143

TABLE V-9
EFFLUENT CHARACTERISTICS WITH APPLICATION OF CONTROLS - POLLUTANT AMOUNTS

Plant Code	See Note	Sampled By	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			
				Cyanide	Cadmium	Chromium	Silver
0021	^{2,3}	Self	64,000 (1,580)	--	--	--	0.16 (0.032)
0045		See Table V-13					
0118		No production information					
0662	^{2,3}	Self	80,300 (1,970)	--	--	--	0.12 (0.025)
1232		Not available					
1330		No production information					
1421		Self	1,300,000 (33,000)	--	--	--	0.27 (0.055)
1465		See Table V-13					
1635	^{2,3}	Self	77,800 (1,910)	--	--	--	0.25 (0.052)
2146		Self	161,000 (3,960)	--	--	--	0.32 (0.066)
2387		Not available					
2465	⁴	Self	192,000 (4,720)	1.0 (0.21)	<0.0039 (8 x 10 ⁻)	--	0.088 (0.018)
2488	⁴	Self	96,100 (2,360)	0.4 (0.08)	<0.002 (4 x 10 ⁻)	--	0.032 (0.0065)
2488	⁴	EPA	478,000 (11,740)	0.4 (0.08)	<0.0098 (0.002)	--	0.18 (0.036)
2714		See Table V-13					
2892		Not available					
3075		Not available					
3437	⁴	Self	111,000 (2,730)	0.26 (0.054)	<0.0024 (5 x 10 ⁻)	--	0.028 (0.0058)
3455		Not available					
3630	^{2,3}	Self	73,000 (1,800)	--	--	--	0.043 (0.0089)
4228	⁴	Self	271,000 (6,660)	1.4 (0.28)	<0.0049 (0.001)	--	0.14 (0.028)

¹ Plant has divided process waste into two or more outfalls. Pollutants summed in proportion to stream flow.
² Represents only portion of total plant discharge of process water.
³ Discharge does not include ferricyanide bleach waste which is contractor hauled.
⁴ Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix is not in sample.
⁵ Plant uses end-of-pipe treatments on portion of process wastewaters.

V-34
144

TABLE V-9
(continued)

Plant Code	See Note	Sampled By	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			
				Cyanide	Cadmium	Chromium	Silver
4229		Not available					
4550	¹	EPA	221,000 (5,425)	0.32 (0.065)	0.0029 (6 x 10 ⁻⁴)	--	0.073 (0.015)
4550	⁴	Self	342,000 (8,400)	0.54 (0.11)	<0.0049 (0.001)	--	0.088 (0.018)
4666	⁴	Self	207,000 (4,070)	1.7 (0.34)	<0.0039 (8 x 10 ⁻⁴)	--	0.068 (0.014)
4849		Not available					
5120	¹	Self	57,000 (1,400)	--	2.8 x 10 ⁻⁴ (5.7 x 10 ⁻⁵) ²	--	0.0013 (2.6 x 10 ⁻⁴)
5359		Not available					
5552	⁴	Self	109,000 (2,670)	1.9 (0.39)	<0.002 (4 x 10 ⁻⁴)	--	0.059 (0.012)
6174	³	Self	49,700 (1,220)	1.0 (0.21)	--	--	0.054 (0.011)
6208		Self	138,000 (3,400)	1.2 (0.24)	--	0.49 (0.10)	0.024 (0.0050)
6208		EPA	102,000 (2,500)	0.014 (0.0028)	0.0020 (4.0 x 10 ⁻⁴)	0.32 (0.066)	0.048 (0.0098)
6237		Not available					
6443		EPA	51,300 (1,260)	0.039 (0.008)	<0.001 (2.1 x 10 ⁻⁴)	0.005 (0.001)	0.17 (0.034)
6582	^{2,3}	Self	92,100 (2,260)	--	--	--	0.13 (0.026)
6726	⁴	Self	200,000 (4,900)	0.76 (0.16)	<0.0039 (8 x 10 ⁻⁴)	--	0.17 (0.034)
7644		Not available					
7781		See Table V-13					
8058		Not available					
8226		Self	176,000 (4,320)	0.63 (0.13)	--	0.16 (0.033)	0.054 (0.011)
9061		Not available					
9297		Not available					
9942		No production information					

V-35
145

¹ Plant has divided process waste into two or more outfalls. Pollutants summed in proportion to stream flow.
² Represents only portion of total plant discharge of process water.
³ Discharge does not include ferricyanide bleach waste which is contractor hauled.
⁴ Plant batch treats waste fix by precipitation for reduction of cyanide. Treated waste fix is not in sample.
⁵ Plant uses end-of-pipe treatments on portion of process wastewaters.

TABLE V-9
(continued)

Plant Code	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)									
	TOC	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS			
0021	--	32.7 (6.7)	--	--	--	--	64.5 (13.2)			
0045	See Table V-13									
0118	No production information									
0662	--	40.0 (8.2)	--	--	--	--	53.2 (10.9)			
1232	Not available									
1330	No production information									
1421	--	40.0 (8.2)	7.32 (1.5)	3.91 (0.80)	--	10.7 (2.2)	--			
1465	See Table V-13									
1635	--	25.4 (5.2)	--	--	--	--	92.3 (18.9)			
2146	--	39.5 (8.1)	--	--	--	0.63 (0.13)	--			
2387	Not available									
2465	--	58.6 (12)	--	0.78 (0.16)	<0.0039 (8 x 10 ⁻⁴)	11.7 (2.4)	357.4 (73.2)			
2488	--	40.5 (8.3)	3.37 (0.69)	2.00 (0.41)	--	30.8 (6.3)	--			
2488	--	22.9 (4.7)	--	0.017 (0.0035)	0.0039 (8 x 10 ⁻⁴)	11.2 (2.3)	187.5 (38.4)			
2714	See Table V-13									
2892	Not available									
3075	Not available									
3437	--	25.4 (5.2)	--	0.15 (0.030)	<0.0024 (5 x 10 ⁻⁴)	0.68 (0.14)	131.8 (27.0)			
3455	Not available									
3630	--	5.37 (1.1)	--	--	--	--	38.1 (7.8)			
4228	--	38.1 (7.8)	--	0.98 (0.20)	<0.0098 (0.002)	12.7 (2.6)	436.0 (89.3)			

V-36
146

TABLE V-9
(continued)

Plant Code	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)							TSS	TDS
	TOC	BOD	Nitrogen-Ammonia	Iron	Lead	Iron	TSS		
4229	Not available								
4550	23.9 (4.9)	38.6 (7.9)	2.05 (0.42)	1.32 (0.27)	0.0098 (0.002)	5.4 (1.1)	430.6 (88.2)		
4550	--	<23.9 (4.9)	--	7.81 (1.6)	0.0098 (0.002)	5.4 (1.1)	612.8 (125.5)		
4666	--	97.7 (20)	--	0.88 (0.18)	<0.0049 (0.001)	5.86 (1.2)	424.8 (87.0)		
4849	Not available								
5120	--	0.024 (0.07) ²	--	--	--	7.8 x 10 ⁻⁵ (0.004) ²	59.8 (3.5) ²		
5359	Not available								
5552	--	1.81 (4.7)	--	0.46 (0.094)	<0.002 (4 x 10 ⁻⁴)	11.7 (2.4)	206.5 (42.3)		
6174	--	24.9 (5.1)	--	--	--	--	43.0 (8.8)		
6208	--	12.7 (2.6)	--	0.059 (0.012)	--	1.66 (0.34)	--		
6208	4.4 (0.91)	7.81 (1.6)	1.32 (0.27)	0.019 (0.0039)	<0.0049 (0.001)	2.29 (0.47)	126.5 (25.9)		
6237	Not available								
6443	15 (3.0)	12 (2.5)	3.6 (0.73)	1.9 (0.38)	--	2.1 (0.44)	--		
6582	--	12.2 (2.5)	--	--	--	--	83.5 (17.1)		
6726	--	32.7 (6.7)	--	0.30 (0.062)	<0.0031 (8 x 10 ⁻⁴)	1.81 (0.37)	155.8 (31.3)		
7644	Not available								
7781	See Table V-13								
8058	Not available								
8226	--	36.6 (7.5)	--	--	--	15.6 (3.2)	--		
9061	Not available								
9297	Not available								
9942	No production information								

V-37
147

TABLE V-9
(continued)

Plant Code	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			Total CN
		BOD	COD	Ag	
0201	160,000 (3,930)	24.9(5.1)	46.4(9.5)	0.12(0.025)	8.3 (1.7)
0202	189,000 (4,640)	38.6(7.9)	98.1(20.1)	0.17(0.034)	
0203	246,000 (6,030)	15.1(3.1)	47.8(9.8)	0.22(0.045)	
0204	93,500 (2,300)	21.5(4.4)	55.2(11.3)	0.47(0.096)	23(4.8)
0205	290,000 (7,120)	126.5(25.9)	250.4(51.7)	1.03(0.21)	48(9.8)
0206	120,000 (2,960)	21.5(4.4)	46.4(9.5)	0.059(0.012)	
0207	50,000 (1,380)	19.0(3.9)	66.9(13.7)	0.98(0.20)	
0208	100,000 (2,450)	33.7(6.9)	199.2(40.8)	1.2(0.25)	
0209	297,000 (7,300)	19.0(3.9)	93.7(19.2)	0.54(0.11)	
0210	115,000 (2,830)	20.0(4.1)	36.6(7.5)	0.088(0.018)	21(4.3)
0211	63,000 (1,550)	10.3(2.1)	30.3(6.2)	0.17(0.034)	
0212	3,290,000 (80,700)	133.3(27.3)	572.2(117.2)	0.83(0.17)	
0213	114,000 (2,810)	15.1(3.1)	31.7(6.5)	0.21(0.049)	
0214	156,000 (3,830)	48.8(10.0)	88.9(18.2)	0.037(0.0075)	370(75)
0215	161,000 (3,960)	21.5(4.4)	66.4(13.6)	0.68(0.14)	4.4(0.90)
0216	13,900,000 (341,000)	139.2(28.5)	488.7(100.1)	6.3(1.3)	
0217	70,000 (1,720)	27.3(5.6)	65.4(13.4)	0.40(0.082)	5.4(1.1)
0218	129,000 (3,180)	34.2(7.0)	113(23.1)	1.4(0.29)	13(2.6)
0219	32,100 (790)	6.3(1.3)	25.9(5.3)	0.83(0.17)	0.59(0.12)
0220	183,000 (4,500)	18.1(3.7)	65.4(13.4)	0.054(0.011)	
0221	63,100 (1,550)	2.8(0.57)	18.1(3.7)	0.34(0.070)	
0222	151,000 (3,700)	19.5(4.0)	73.2(15.0)	0.68(0.14)	
0223	32,500 (800)	17.1(3.5)	52.7(10.8)	0.25(0.051)	
0224	72,400 (1,780)	18.1(3.7)	44.9(9.2)	0.073(0.015)	7.3(1.5)
0225	83,500 (2,050)	17.1(3.5)	48.3(9.9)	0.15(0.031)	
0226	114,000 (2,800)	21.5(4.4)	62.5(12.8)	0.23(0.048)	2.1(0.43)
0227	344,000 (8,460)	81.5(16.7)	154.8(31.7)	0.88(0.18)	8.3(1.7)
0228	20,900 (510)	1.6(0.33)	6.35(1.3)	0.034(0.007)	18(3.6)
0229	817,000 (200,000)	44.9(9.2)	114.3(23.4)	0.82(0.167)	
0230	111,000 (2,730)	39.1(8.0)	104.0(21.3)	0.80(0.163)	
0231	86,200 (2,120)	4.9(1.0)	23.9(4.9)	0.044(0.009)	
0232	280,000 (6,880)	105.5(21.6)	199.7(40.9)	0.13(0.027)	63(0.26)
0233	193,000 (4,740)	43.0(8.8)	122.1(25.0)	0.049(0.010)	0.59(0.12)
0234	419,000 (10,300)	66.4(13.6)	125.4(26.3)	0.059(0.012)	2.59(0.53)
0235	203,000 (4,980)	40.5(8.3)	211.9(43.4)	0.19(0.039)	1.37(0.28)
0236	141,000 (3,470)	10.7(2.2)	38.5(7.9)	0.088(0.018)	0.59(0.12)
0237	252,000 (6,190)	42.5(8.7)	316.9(64.9)	0.14(0.029)	1.37(0.28)

148

TABLE V-10
TREATMENT TECHNOLOGIES USED BY PHOTOPROCESSORS SURVEYED

Plant Code	Equalization	Neutralization	Aeration	Ozonation	Flocculation	Precipitation	Clarification	Chlorination	Settling	Filtration	Reverse Osmosis
0045							X				
1465											
2387									X		
2714	X	X (wash water only)									X
3075									X		
3455	X				X	X	X	X	X	X	
4229	X								X		
4550					X	X (only waste fix containing FeCN)			X		
4849											
7781			X	X		X			X	X	X
9297	X		X						X		

~~139~~
149

TABLE V-11
 SAMPLING OF IN-PROCESS CONTROLS AND END-OF-PIPE TREATMENTS

Code	Sampled Stream Description	Control Type	Date	Pollutant Concentration, mg/liter												
				Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Phenols	Iron	Lead	TSS	TSS		
1465	Influent to Ozonation- (Concentrated chemicals only) Ozonation Effluent	End-of-pipe treatment for reduction of oxygen demand		<0.02	3,700	<0.05	1.35	0.55	4,928	--	228	--	2	17,900		
				<0.02	2,990	<0.05	0.35	0.37	3,232	--	111	--	2	13,900		
2714	Influent to RO (paper wash) RO Permeate (paper wash) Influent to RO (film wash) RO Permeate (film wash)	End-of-pipe treatment on wash water	8-7	0.04	420	0.017	0.08	6.3	--	--	112	0.09	20	1,895		
				<0.01	178	<0.02	<0.02	0.04	605	0.27	1.79	<0.05	14.5	182		
				0.70	24	<0.02	0.22	0.99	--	<0.02	5.1	<0.05	11.8	615		
				0.03	6.9	<0.02	0.02	<0.02	7.9	<0.02	0.28	<0.05	9	180		
4550	Fix Waste before SR Influent to Ferro Precipita- tion (Fix waste after SR) Ferro Precipitation Effluent	SR on fix and end- of-pipe treatment for reduction of cyanide	7-77	4,310	--	--	--	576	--	--	--	--	72	87,100		
				4,440	--	--	--	21	--	--	--	--	217	92,700		
				2.0	--	--	--	8.4	--	--	--	--	1,800	119,700		
7781	Film Wash (except after fix)-partial influent to aeration Influent to RO RO Permeate RO Concentrate (Influent to Metals Removal) Metals Removal Effluent- partial influent to aeration Influent to Ozonation Ozonation Effluent - partial influent to aeration	Segregation of wastewater Wash water recycle SR and end-of-pipe treatment for reduction of heavy metals End-of-pipe treatment	8-77	--	153	0.017	0.04	1.12	--	0.73	39	0.19	103	1,210		
				--	1,100	1.1	<0.05	68	--	17	80	0.27	3.7	5,950		
				--	635	0.25	<0.02	16	--	18.3	26	0.08	<1	3,060		
				--	3,710	4.9	0.72	57	--	11.3	340	1.8	34	26,480		
				--	3,450	0.06	0.16	0.08	--	4.9	5.8	0.07	19.4	53,100		
				--	2,175	0.04	<0.04	1.2	3,250	7.2	2.5	0.07	253	9,155		
				--	2,400	0.03	<0.03	1.15	3,250	3.21	2.6	0.06	12.2	6,565		

V-40
150

TABLE V-12
EFFLUENT CHARACTERISTICS AFTER APPLICATION OF END-OF-PIPE TREATMENTS - POLLUTANT CONCENTRATIONS

Plant Code	Sample Information			Pollutant Concentration, mg/liter										
	Description	Date	By	Cyanide	TOC	Cadmium	Chromium	Silver	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
0045	Avg. of 3 daily composites	74-76	Self	1.27	--	--	--	1.24	--	--	--	--	--	--
1465	Several values from period ¹	1974	Self	1.4	107	--	--	0.72	155	802 ¹	5.1	--	6.4	708
1465	Single 24-hr. Composite ¹	11-74	EPA	0.054	60.8	<0.05	0.05	0.19	57	15	5.5	--	1	471
2714	Avg. of two values ²	1977	Self	0.2	--	--	--	0.04	9.9	--	--	--	--	216
2714	Grabs from 38,000 liter tanks ¹	8-77	EPA	1.1	672	0.017	0.04	2.7	1,124	350	39.9	0.06	46.5	3,152
7781	Avg. of 3 monthly averages of daily values	1977	Self	--	--	0.20	--	5.6	112	--	17	0.19	41	--
7781	Avg. of 3 24-hr. FP Composites	7-77	EPA	0.04	153	0.03	0.02	1.7	155	57	2.6	0.04	12	3,356

V-44
151

¹ Plant has divided process wastewaters into two or more outfalls. Pollutants summed in proportion to stream flow.
² Represents only portion of total plant discharge of process water.

TABLE V-13

EFFLUENT CHARACTERISTICS AFTER APPLICATION OF END-OF-PIPE TREATMENTS - POLLUTANT AMOUNTS

Plant Code	See Note	Sampled By	Hydraulic Load, liters/1,000 sq m (gal/1,000 sq ft)	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)			
				Cyanide	Cadmium	Chromium	Silver
0045	2	Self	288,000 (7,060)	--	--	--	0.36 (0.073)
1465	1,3	Self	286,000 (7,030)	11 (2.2)	--	--	0.21 (0.042)
1465	1,3	EPA	286,000 (7,030)	4.2 (0.86)	<0.015 (0.003)	--	0.054 (0.011)
2714	1,4	Self	15,500 (380)	0.63 (0.13)	--	--	5 x 10 ⁻⁴ (1 x 10 ⁻⁴)
2714	1,3	EPA	23,900 (587)	8.3 (1.7)	4.1 x 10 ⁻⁴ (8.3 x 10 ⁻⁵)	--	0.063 (0.013)
7781	?	Self	7,500 (184)	--	0.0015 (3 x 10 ⁻⁴)	--	0.042 (0.0085)
7781	?	EPA	5,010 (123)	--	1.5 x 10 ⁻⁴ (3 x 10 ⁻⁵)	--	0.0088 (0.0018)

V-42
152

- 1 - Plant uses end-of-pipe treatments on portion of process wastewaters.
- 2 - Plant uses end-of-pipe treatments on all process wastewaters.
- 3 - Plant has divided process waste into two or more outfalls. Pollutants summed in proportion to stream flow.
- 4 - Represents only portion of total plant discharge of process water.

TABLE V-13
(continued)

Plant Code	Pollutant Amount, kg/1,000 sq m (lb/1,000 sq ft)						
	TOC	BOD	Nitrogen-Ammonia	Iron	Lead	TSS	TDS
0045	--	--	--	--	--	--	--
1465	30.7 (6.3)	44.4 (9.09)	2.13 (0.66) ²	1.46 (0.30)	--	1.86 (0.38)	202.6 (41.5)
1465	17.4 (3.57)	16.1 (3.3)	4.30 (0.88)	1.56 (0.32)	--	0.29 (0.06)	134.8 (27.6)
2714	--	0.1 (0.03)	--	--	--	--	3.4 (0.69)
2714	16.1 (3.29)	26.9 (5.51)	8.35 (1.71)	0.95 (0.195)	0.0015 (3 x 10 ⁻⁴)	1.11 (0.228)	75.2 (15.4)
7781	--	0.83 (0.17)	--	0.13 (0.026)	0.0015 (3 x 10 ⁻⁴)	0.31 (0.063)	--
7781	0.78 (0.16)	0.77 (0.158)	0.28 (0.058)	0.013 (0.0027)	2 x 10 ⁻⁴ (4 x 10 ⁻⁵)	0.059 (0.012)	16.8 (3.44)

~~V-13~~
153

154

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

The Agency is concerned over potential discharges of toxic pollutants from industrial sources. A comprehensive effort was conducted to determine if these pollutants are present in wastewaters from photographic processing. The toxic pollutants are listed in Table VI-1. The conventional parameters listed in Table VI-2 and non-conventional parameters listed in Table VI-3 were also selected to be sought in the field data collection program. In addition, related published data and NPDES permit applications for direct discharges in this industry were examined to assist in this determination.

The wastewater characterization detailed in the previous section has been reviewed to determine what wastewater constituents are contributed to photoprocessing wastewater in significant quantities. A toxic pollutant was considered significant unless one or more of the following was true:

- (a) the pollutant was not detected,
- (b) its presence was due to incoming water, or
- (c) it was present in concentrations below current water quality criteria.

TABLE VI-1
Toxic Pollutants

acenaphthene	4-bromophenyl phenyl ether
acrolein	bis(2-chloroisopropyl) ether
acrylonitrile	bis(2-chloroethoxy) methane
benzene	methylene chloride (dichloro- methane)
benzidine	methyl chloride (chloromethan)
carbon tetrachloride (tetrachloro- methane)	methyl bromide (bromomethane)
chlorobenzene	bromoform (tribromomethane)
1,2,4-trichlorobenzene	dichlorobromomethane
hexachlorobenzene	trichlorofluoromethane
1,2-dichloroethane	dichlorodifluoromethane
1,1,1-trichloroethane	chlorodibromomethane
hexachloroethane	hexachlorobutadiene
1,1-dichloroethane	hexachlorocyclopentadiene
1,1,2-trichloroethane	isophorone
1,1,2,2-tetrachloroethane	naphthalene
chloroethane	nitrobenzene
bis(chloromethyl) ether	2-nitrophenol
bis(2-chloroethyl) ether	4-nitrophenol
2-chloroethyl vinyl ether (mixed)	2,4-dinitrophenol
2-chloronaphthalene	4,6-dinitro-o-cresol
2,4,6-trichlorophenol	N-nitrosodimethylamine
parachlorometa cresol	N-nitrosodiphenylamine
chloroform (trichloromethane)	N-nitrosodi-n-propylamine
2-chlorophenol	pentachlorophenol
1,2-dichlorobenzene	phenol
1,3-dichlorobenzene	bis(2-ethylhexyl) phthalate
1,4-dichlorobenzene	butyl benzyl phthalate
3,3 ¹ -dichlorobenzidine	di-n-butyl phthalate
1,1-dichloroethylene	di-n-octyl phthalate
2,4-dichlorophenol	diethyl phthalate
1,2-dichloropropane	dimethyl phthalate
1,2-dichloropropylene (1,3-dichloro- propene)	benzo(a)anthracene (1,2-ben- zanthracene)
2,4-dimethylphenol	benzo(a)pyrene (3,4-benzo- pyrene)
2,4-dinitrotoluene	3,4-benzofluoranthene
2,6-dinitrotoluene	benzo(k)fluoranthene
1,2-diphenylhydrazine	(11,12-benzofluoranthene)
ethylbenzene	chrysene
fluoranthene	acenaphthylene
4-chlorophenyl phenyl ether	

TABLE VI-1 (continued)

anthracene	a-BHC-Alpha
benzo(ghi)perylene(1,12-benzoperylene)	b-BHC-Beta
fluorene	r-BHC-(lindane)Gamma
phenanthrene	g-BHC-Delta
dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)	PCB-1242 (Arochlor 1242)
indeno(1,2,3-cd) pyrene	PCB-1254 (Arochlor 1254)
(2,3-o-phenylenepyrene)	PCB-1221 (Arochlor 1221)
pyrene	PCB-1232 (Arochlor 1232)
tetrachloroethylene	PCB 1248 (Arochlor 1248)
toluene	PCB-1260 (Arochlor 1260)
trichloroethylene	PCB-1016 (Arochlor 1016)
vinyl chloride (chloroethylene)	toxaphene
aldrin	antimony (total)
dieldrin	arsenic (total)
chlordane	asbestos (fibrous)
4,4 ¹ -DDT	beryllium (total)
4,4 ¹ -DDE(p,p ¹ -DDX)	cadmium (total)
4,4 ¹ -DDD(p,p ¹ -TDE)	chromium (total)
a-endosulfan-Alpha	copper (total)
b-endosulfan-Beta	cyanide (total)
endosulfan sulfate	lead (total)
endrin	mercury (total)
endrin aldehyde	nickel (total)
heptachlor	selenium (total)
heptachlor epoxide	silver (total)
	thallium (total)
	zinc (total)

TABLE VI-2
Conventional Pollutants

pH
BOD
COD
Oil and Grease
Suspended Solids

TABLE VI-3
Non-Conventional Pollutants

Acidity	Sulfate
Alkalinity	Sulfite/Thiosulfate
Carbon, organic (TOC)	Surfactants
Chlorinated Hydrocarbons	Thiocyanate
Color (units)	Turbidity (units)
Cyanide (am. chlorin.)	Aluminum
DO	Barium
Fe(CN) ₆	Boron
Fluoride	Calcium
Halides	Chromium ⁶⁺
Hydroquinone	Cobalt
Nitrogen-	Iron
Ammonia	Magnesium
Phenols	Manganese
Silica	Molybdenum
Solids -	Potassium
Total	Sodium
Dissolved	Tin
Volatile	Titanium
Specific conductance	

Wastewaters from plants 6208, 2714, 4550 and 7781 were examined for toxic pollutants. No organic toxic pollutants were found except 1,2-diphenylhydrazine, which was found (200 ug/l) in one stream at plant 2714. This chemical was found in the reverse osmosis permeate but was absent in the reverse osmosis concentrate, raising the possibility that its presence in the permeate was an anomaly. This pollutant was not found at any other plant. The organic priority pollutants were measured to a detectability limit of 20 ug/l by gas chromatograph-mass spectrometer analysis.

Pesticides were found at low levels at four of the five plants. Amounts varied from the detection limit up to 1.6 ug/l. Similar amounts of pesticides were also found in the incoming water supply in these plants. The quantitation limit for pesticides is 0.1 ug/l with the instrumentation used. The single effluent streams from plants 6208, 4550 and 7781 and all three outfalls for plant 2714 were analyzed for asbestos, but none was found.

The following toxic metals were not found above their detectable limits in plant effluents:

<u>Metal</u>	<u>Detectable Limit, mg/l</u>
Arsenic	0.002
Beryllium	0.005
Copper	0.010
Mercury	0.0002
Nickel	0.020
Selenium	0.002
Thallium	0.100

Antimony and zinc were found in concentrations equivalent to concentrations in incoming water supply or equal to, or less than, current water quality criteria.

A discussion of those conventional and toxic pollutant parameters which were found in significant quantity follows. Table VI-4 lists these parameters.

TABLE VI-4
Pollutants Found in Significant Quantities in
Effluents from Photographic Processing Plants

<u>Toxic</u>	<u>Conventional</u>	<u>Non-Conventional</u>
Cadmium	pH	Boron
Chromium	BOD	Dissolved Solids
Cyanide, total	COD	Halides
Lead		Iron
Silver		Nitrogen, ammonia
		Phenols
		Sulfate
		TOC

DESCRIPTION OF POLLUTANT PARAMETERS OF SIGNIFICANCE

I. POLLUTANT PROPERTIES

Acidity and Alkalinity - pH

Although not a specific pollutant, pH is related to the acidity or alkalinity of a wastewater stream. It is not a linear or direct measure of either; however, it may

properly be used as a surrogate to control both excess acidity and excess alkalinity in water. The term pH is used to describe the hydrogen ion - hydroxyl ion balance in water. Technically, pH is the hydrogen ion concentration or activity present in a given solution. pH numbers are the negative logarithm of the hydrogen ion concentration. A pH of 7 generally indicates neutrality or a balance between free hydrogen and free hydroxyl ions. Solutions with a pH above 7 indicate that the solution is alkaline, while a pH below 7 indicates that the solution is acid.

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

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

Photographic processing wastewaters from the individual processing steps are both basic and acidic. For example, developers are basic and the stop and fix solutions are acidic. When waste streams from these solutions are combined in the plant discharge, the different streams tend to neutralize each other. Overall plant discharges in this industry are generally in the pH range of 6 to 9 with most in the range of 7 to 8.5.

* The term toxic or toxicity is used herein in the normal scientific sense of the word and not as a specialized term referring to Section 307(a) of the Act.

Acidity is defined as the quantitative ability of a water to neutralize hydroxyl ions. It is usually expressed as the calcium carbonate equivalent of the hydroxyl ions neutralized. Acidity should not be confused with pH value. Acidity is the quantity of hydrogen ions which may be released to react with or neutralize hydroxyl ions while pH is a measure of the free hydrogen ions in a solution at the instant the pH measurement is made. A property of many chemicals, called buffering, may hold hydrogen ions in a solution from being in the free state and being measured as pH. The bond of most buffers is rather weak, and hydrogen ions tend to be released from the buffer as needed to maintain a fixed pH value.

Highly acid waters are corrosive to metals, concrete, and living organisms, exhibiting the pollutional characteristics outlined above for low pH waters. Depending on buffering capacity, water may have a higher total acidity at pH values of 6.0 than other waters with a pH value of 4.0.

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

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

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

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

Total Suspended Solids

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

Suspended solids in water interfere with many industrial processes, cause foaming in boilers and incrustations on equipment exposed to such water, especially as the temperature rises. They are undesirable in process water used in the manufacture of steel, in the textile industry, in laundries, in dyeing, and in cooling systems. Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often damaging to the life in water. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a food source for sludgeworms and associated organisms.

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

Suspended solids are not normally a problem in this industry. However, suspended solids are generated during some recovery operations such as precipitation of silver sulfide and ferro/ferricyanides. These solids are sometimes recovered for recovery of silver or reuse, respectively.

II. POLLUTANT MATERIALS

Ammonia (NH₃)

Ammonium compounds are used in the photoprocessing industry as constituents in some fix, bleach-fix, and stabilizer solutions. The ammonium ion can be present in these solutions at concentrations of 10 to 100 grams per liter and be present in the plant effluent in concentrations up to 150 mg/l.

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

Ammonia exists in its non-ionized form only at higher pH levels and is most toxic in this state. The lower the pH, the more ionized ammonia is formed, and its toxicity decreases. Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO₃) by nitrifying bacteria. Nitrite (NO₂), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit. Ammonia can exist in several other chemical combinations including ammonium chloride and other ammonia salts.

Nitrates are considered to be among the objectionable components of mineralized waters. Excess nitrates cause irritation to the gastrointestinal tract, causing diarrhea and diuresis. Methemoglobinemia, a condition characterized by cyanosis which can result in infant and animal deaths, can be caused by high nitrate concentrations in waters used for feeding. Evidence exists that ammonia exerts a toxic effect on all aquatic life depending upon the pH, dissolved

oxygen level, and the total ammonia concentration in the water. A significant oxygen demand can result from the microbial oxidation of ammonia. Approximately 4.5 grams of oxygen are required for every gram of ammonia that is oxidized. Ammonia can add to eutrophication problems by supplying nitrogen to aquatic life. Ammonia can be toxic, exerts an oxygen demand, and contributes to eutrophication.

Boron (B) Boron compounds, in the form of borates, are used in developers, bleaches, and fixers in concentrations up to one hundred grams per liter. After mixing of the various waste solutions, the amount of boron in the plant effluent generally ranges from 1 to 10 mg/l.

Never found in nature in its elemental form, boron occurs as sodium borate (borax) or as calcium borate (colemanite) in mineral deposits and natural waters of Southern California and Italy. Elemental boron is used in nuclear installations as a shielding material (neutron absorber). It is also used in metallurgy to harden other metals.

Boric acid and boron salts are used extensively in industry for such purposes as weatherproofing wood, fireproofing fabrics, manufacturing glass and porcelain, and producing leather, carpets, cosmetics, and artificial gems. Boric acid is used as a bactericide and fungicide and boron, in the form of boron hydrides or borates, is used in high energy fuels.

Boron is present in the ordinary human diet at about 10 to 20 mg/day, with fruits and vegetables being the largest contributors. In food or in water, it is rapidly and completely absorbed by the human system, but it is also promptly excreted in urine. Boron in drinking water is not generally regarded as a hazard to humans. It has been reported that boron concentrations up to 30 mg/l are not harmful.

Bromide (Br)

Bromides are derived from hydrobromic acid (HBr). Bromide properties are similar to those of chlorides and iodides. Bromides are usually produced from bromine, which in turn is obtained from salt brines or sea water.

Bromides are used in medicine as sedatives in the treatment of nervous disorders. Silver bromide is used in photographic films and paper, and bromide compounds are present in the formulations of bleaches.

Cadmium (Cd)

Cadmium occurs in some, but not all photoprocessing facilities, because it is an ingredient in some sensitized products. The cadmium compounds are at least partially removed during the development portion of the process and are primarily found in the waste developer.

Cadmium is a relatively rare element that is seldom found in sufficient quantities in a pure state to warrant mining or extraction from the earth's surface. It is found in trace amounts of about 1 ppm throughout the earth's crust. Cadmium is, however, a valuable by-product of zinc production.

Cadmium is used primarily as a metal plating material and can be found as an impurity in the secondary refining of zinc, lead, and copper. Cadmium is also used in the manufacture of primary and storage batteries and as a neutron adsorber in nuclear reactors. Other uses of cadmium are in the production of pigments, phosphors, semi-conductors, electrical conductors, and special purpose low temperature alloys.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious progressive chronic poisoning in mammals, fish, and probably other animals because the metal is not excreted. Cadmium could form organic compounds which might lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms also.

Toxic effects of cadmium on man have been reported from throughout the world. Cadmium is normally ingested by humans through food and water and also by breathing air contaminated by cadmium. Cadmium in drinking water supplies is extremely hazardous to humans, and conventional treatment, as practiced in the United States, does not remove it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe

bone and kidney syndrome in Japan has been associated with the ingestion of as little as 600 μ g/day of cadmium. The allowable cadmium concentration in drinking water is set as low as 0.01 mg/l in the U.S. and as high as 0.10 mg/l in Russia.

Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms, particularly mollusks which accumulate cadmium in calcareous tissues and in the viscera. A concentration factor of 1,000 for cadmium in fish muscle has been reported, as have concentration factors of 3,000 in marine plants, and up to 29,600 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

Chlorides

Chlorides are found in practically all natural waters. They may be: (a) of natural mineral origin or derived from a sea-water contamination of underground supplies, (b) salts spread on fields for agricultural purposes, (c) human or animal sewage, or (d) industrial effluents, such as those from paper works, galvanizing plants, water softening plants, oil wells, and petroleum refineries.

The human tolerance for chlorides varies with climate and exertion. Chlorides lost through perspiration are replaced by chlorides in either the diet or drinking water. From hot dry areas, there are reports that chloride concentrations up to almost 900 mg/l have not been harmful. Chloride concentrations of 1,500 mg/l are reported to be safe for cattle, sheep, swine and chickens. Also, 2,000 mg/l of chloride has been reported as not harmful to some fish.

Because of their non-toxic nature, chlorides are not selected as a pollutant parameter requiring the establishment of a limitation.

Chromium (Cr)

Sodium and potassium dichromate are principal constituents of certain bleaches used primarily in the color movie print

film process. These compounds in combination with bromide ions oxidize the developed silver to silver bromide. A dichromate bleach may also be used in the black and white reversal process. Again, the primary application for this process is in the movie industry.

Chromium is an elemental metal usually found as a chromite (FeCr_2O_4). The metal is normally processed by reducing the oxide with aluminum. Chromium and its compounds are used extensively throughout industry. It is used to harden steel and as an ingredient in other useful alloys. Chromium is also used in the electroplating industry as an ornamental and corrosion resistant plating on steel and can be used in pigments and as a pickling acid (chromic acid). It is used in certain chromate bleaches in the photographic processing industry.

The two most prevalent chromium forms found in industry wastewaters are hexavalent and trivalent chromium. Dichromate compounds used in the photographic processing industry are hexavalent chromium compounds which are partially reduced to the trivalent form during use. Chromium can exist as either trivalent or hexavalent compounds in raw waste streams, although most of the hexavalent chromium is reduced to the trivalent form when mixed with other photographic processing wastes, particularly sulfites and thiosulfates. Hexavalent chromium treatment involves reduction to the trivalent form prior to removal of chromium from the waste stream as a hydroxide precipitate.

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

The toxicity of chromium salts to fish and other aquatic life varies widely with the species, temperature, pH, valence of the chromium and synergistic or antagonistic effects, especially those of hard water. Studies have shown

that trivalent chromium is more toxic to fish of some types than hexavalent chromium. Other studies have shown opposite effects. Fish food organisms and other lower forms of aquatic life are extremely sensitive to chromium, and it also inhibits the growth of algae. Therefore, both hexavalent and trivalent chromium must be considered harmful to particular fish or organisms.

Chromium is not destroyed when treated by a POTW (although the oxidation state may change), and either passes through to the POTW effluent or is incorporated into the POTW sludge. Both oxidation states can cause POTW treatment inhibition and can also limit the usefulness of municipal sludge. Hexavalent and trivalent chromium both cause toxic effects in a wide variety of organisms including aquatic species and humans. Chromium which passes through a POTW becomes a potential drinking and bathing water contaminant. Hexavalent chromium is a known human carcinogen, and is generally the more toxic of the two oxidation states. As a result of these considerations, chromium pretreatment standards must be the same as discharge limitations for direct discharge.

Cyanide (CN)

Cyanide is a compound that is widely used in industry primarily as sodium cyanide (NaCN) or hydrocyanic acid (HCN). The major use of cyanides is in the electroplating industry where cyanide baths are used to hold ions such as zinc and cadmium in solution. Cyanides in various compounds are also used in steel plants, chemical plants, textile dyeing, and ore processing.

Cyanides in the form of an iron-cyanide complex are used in the photographic processing industry. This complex, usually sodium or potassium ferricyanide, is a major constituent of a commonly used color bleach which oxidizes the metallic silver image to a silver halide. During the process a portion of the ferricyanide ions is reduced to ferrocyanide, and the waste bleach contains a mixture of ferri-ferrocyanide (hexacyanoferrate) ions.

The hexacyanoferrate ions exhibit a low order of toxicity to aquatic species. Acute static bioassay tests performed by exposing fathead minnows (*Pimephales promelas*) to various

concentrations of the ferrocyanide ion resulted in a 96-hour LC₅₀ value of greater than 100 ppm. (The 96-hour LC₅₀ value is the chemical concentration that will cause a 50 percent mortality of the test species after the 96-hour exposure.) Similar tests with lower forms of aquatic life did show greater sensitivity, i.e., 96-hour LC₅₀ values of 0.1 to 1 ppm for crustaceans (*Daphnia magna*) and algae growth was inhibited at ferrocyanide concentrations of 1 to 10 ppm. It has been shown that the hexacyanoferrate ions are photochemically active and readily release the cyanide ion with sunlight exposure. Bioassay tests with 8,000 foot candles of simulated sunlight resulted in 50 percent minnow fatalities in about five hours at a 100 ppm ferrocyanide concentration. This photochemical effect is of concern for those facilities which use ferricyanide bleach and discharge the wastewater directly to surface waters.

The large majority of photoprocessing facilities discharge to POTW's. Laboratory and on-site treatment plant tests have shown that the hexacyanoferrate ions cause no adverse effects on the biomass and are resistant to biological degradation. The treatment plant removal efficiency was reported to be greater than 60 percent. The hexacyanoferrate ions are probably precipitated in the presence of iron, zinc, or calcium ions and are combined with the waste sludge.

Land disposal is a common disposal method for POTW sludges. The fate of the hexacyanoferrates under land disposal conditions has been evaluated with leachate tests in the laboratory. Such tests were performed using several soil types and several test sludges ranging in total cyanide content from 9 to 37,000 mg/kg (dry basis). Evaluation of the elutriate showed no release, and column tests showed that the hexacyanoferrates were released from the sludge in particulate form and were bound within the soil by adsorption and filtration.

Of all the cyanides, hydrogen cyanide (HCN) is probably the most acutely lethal compound. HCN dissociates in water to hydrogen ions and cyanide ions in a pH dependent reaction. The cyanide ion is less acutely lethal than HCN. The relationship of pH to HCN shows that as the pH is lowered to below 7, there is less than 1 percent of the cyanide molecules in the form of the CN ion and the rest is present

as HCN. When the pH is increased to 8, 9, and 10, the percentage of cyanide present as CN ion is 6.7, 42 and 87 percent, respectively. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two to threefold increase in the rate of the lethal action of cyanide.

In the body, the CN ion, except for a small portion exhaled, is rapidly changed into a relatively non-toxic complex (thiocyanate) in the liver and eliminated in the urine. There is no evidence that the CN ion is stored in the body. The safe ingested limit of cyanide has been estimated at something less than 18 mg/day, part of which comes from normal environment and industrial exposure. The average fatal dose of HCN by ingestion by man is 50 to 60 mg. It has been recommended that a limit of 0.2 mg/l cyanide not be exceeded in public water supply sources.

The harmful effects of the cyanides on aquatic life are affected by the pH, temperature, dissolved oxygen content, and the concentration of minerals in the water. The biochemical degradation of cyanide is not affected by temperature in the range of 10°C to 35°C while the toxicity of HCN is increased at higher temperatures.

On lower forms of life and organisms, cyanide does not seem to be as toxic as it is toward fish. The organisms that digest BOD were found to be inhibited at 1.0 mg/l and at 60 mg/l although the effect is more one of delay in exertion of BOD than total reduction.

Dissolved Solids

In natural waters, the dissolved solids are mainly carbonates, chlorides, sulfates, phosphates, and to a lesser extent, nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese, and other substances. The summation of all individual dissolved solids is commonly referred to as total dissolved solids.

Many communities in the United States and in other countries use water supplies containing 2,000 to 4,000 mg/l of dissolved salts, when no better water is available. Such waters are not palatable, may not quench thirst, and may

have a laxative action on new users. Waters containing more than 4,000 mg/l of total salts are generally considered unfit for human use, although in hot climates such higher salt concentrations can be tolerated. Waters containing 5,000 mg/l or more are reported to be bitter and act as a bladder and intestinal irritant. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l.

Limiting concentrations of dissolved solids for fresh-water fish may range from 5,000 to 10,000 mg/l, depending on species and prior acclimatization. Some fish are adapted to living in more saline waters, and a few species of fresh-water forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l. Fish can slowly become acclimatized to higher salinities, but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil well brines. Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness on metals.

Waters with total dissolved solids (TDS) concentrations higher than 500 mg/l have decreasing utility as irrigation water. At 5,000 mg/l, water has little or no value for irrigation.

Dissolved solids in industrial water uses can cause foaming in boilers and can cause interferences with cleanliness, color, or taste of many finished products. High concentrations of dissolved solids also tend to accelerate corrosion. Most of the solids present in photoprocessing wastewater are dissolved.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and to the water temperature. This property is frequently used as a substitute method of quickly estimating the dissolved solids concentration.

~~VI-17~~
171

Iron (Fe)

Iron is an abundant metal found in the earth's crust. The most common iron ore is hematite from which iron is obtained by reduction with carbon. Other forms of commercial ores are magnetite and taconite. Pure iron is not often found in commercial use, but it is usually alloyed with other metals and minerals, the most common being carbon.

Iron is the basic element in the production of steel and steel alloys. Iron with carbon is used for casting of major parts of machines, and it can be machined, cast, formed, and welded. Ferrous iron is used in paints, while powdered iron can be sintered and used in powder metallurgy. Iron compounds are also used to precipitate other metals and undesirable minerals from industrial wastewater streams. The dissolved iron present in photoprocessing wastewaters comes from two sources. Iron compounds are used as bleaches, and iron is added to wastewater by metallic replacement silver recovery processes.

Iron is chemically reactive and corrodes rapidly in the presence of moist air and at elevated temperatures. In water and in the presence of oxygen, the resulting products of iron corrosion may be pollutants in water. Natural pollution occurs from the leaching of soluble iron salts from soil and rocks and is increased by industrial wastewater from pickling baths and other solutions containing iron salts.

Corrosion products of iron in water cause staining of porcelain fixtures, and ferric iron combines with the tannin to produce a dark violet color. The presence of excessive iron in water discourages cows from drinking and, thus, reduces milk production. High concentrations of ferric and ferrous ions in water kill most fish introduced to the solution within a few hours. The killing action is attributed to coatings of iron hydroxide precipitates on the gills. Iron oxidizing bacteria are dependent on iron in water for growth. These bacteria form slimes that can affect the aesthetic values of bodies of water and cause stoppage of flows in pipes.

Iron is an essential nutrient and micronutrient for all forms of growth. Drinking water standards in the U.S. have

set a recommended limit of 0.3 mg/l of iron in domestic water supplies based not on the physiological considerations, but rather on aesthetic and taste considerations of iron in water.

Lead (Pb)

Lead is used in various solid forms both as a pure metal and in several compounds. Lead appears in some natural waters, especially in those areas where mountain limestone and galena are found. Lead can also be introduced into water from lead pipes by the action of the water on the lead. Lead is not knowingly added to process wastewater in this industry.

Lead is a toxic material that is foreign to humans and animals. The most common form of lead poisoning is called plumbism. Lead can be introduced into the body from the atmosphere containing lead or from food and water. Lead cannot be easily excreted and is cumulative in the body over long periods of time, eventually causing lead poisoning with the ingestion of an excess of 0.6 mg per day over a period of years. It has been recommended that 0.05 mg/l lead not be exceeded in public water supply sources.

Chronic lead poisoning has occurred among animals at levels of 0.18 mg/l of lead in soft water and by concentrations under 2.4 mg/l in hard water. Farm animals are poisoned by lead more frequently than any other poison. Sources of this occurrence include paint and water with the lead in solution as well as in suspension. Each year thousands of wild water fowl are poisoned from lead shot that is discharged over feeding areas and ingested by the water fowl. The bacterial decomposition of organic matter is inhibited by lead at levels of 0.1 to 0.5 mg/l.

Fish and other marine life have had adverse effects from lead and salts in their environment. Experiments have shown that small concentrations of heavy metals, especially of lead, have caused a film of coagulated mucus to form first over the gills and then over the entire body probably causing suffocation of the fish. Toxicity of lead is increased with a reduction of dissolved oxygen concentration in the water.

Phenols

Phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in domestic and industrial wastewater and in drinking water supplies. Chlorination of such waters can produce odoriferous and objectionable tasting chlorophenols.

Although described in the technical literature simply as phenols, the phenol waste category can include a wide range of similar chemical compounds. In terms of pollution control, reported concentrations of phenols are the result of a standard methodology which measures a general group of similar compounds rather than being based upon specific identification of the single compound, phenol (hydroxybenzene). Some of the compounds used in photoprocessing which might be identified as phenols will not respond to standard analytical tests for phenols and do not impart taste to water after chlorination.

Phenols are used in some cutting oils and in the molding of plastics. Cutting fluids can contain phenolic compounds since these materials are normal constituents of hydrocarbon mixtures. In addition, phenolic compounds are added to oils as preservatives or for odor control. They also are found in the wastewaters from the petroleum industry and from certain products of the organic chemical industry.

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

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

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

Silver (Ag)

The emulsion on photographic film and paper contains as a principal ingredient various silver halides which form or assist in the formation of the photographic image. During processing a portion (black and white materials) or all (color materials) of the silver is removed from the emulsion by the fix solution. A principal constituent of the fix solution is the thiosulfate ion which forms a complex with silver. The silver thiosulfate complex is stable (it has a dissociation constant of 3.5×10^{-14}) and non-toxic to fish (bioassay test showed no effect on fathead minnows after 96 hours of exposure to the silver thiosulfate complex at concentrations up to 50 mg/l as silver).

Since the large majority of the photoprocessing industry discharges to POTW's, the major concern is the fate of the complex after secondary treatment. Studies have shown that the secondary treatment microorganisms convert the complex to silver sulfide and some metallic silver, most of which is removed from the wastewater stream by settling. The portion that remains with the wastewater exists as colloidal suspensions of silver sulfide and silver and a small fraction of soluble ionic silver. Silver sulfide is insoluble under normal environmental conditions. Bioassay tests have shown it to be non-toxic to fathead minnows. Dynamic 96-hour LC_{50} tests for silver sulfide showed no fatalities at a maximum total silver concentration of 250 ppm.

The silver sulfide and silver that settles is removed from the treatment plant as a constituent of the sludge. Land disposal by landspreading or landfilling is a common disposal method for POTW sludges. Laboratory leachate testing on test sludges containing silver in concentrations from 19 to 83,000 mg/kg (dry) showed no release of silver to the elutriate. Column tests indicated that the silver was effectively bound by the various soil types.

VI-21
175

Silver is a soft, lustrous white metal that is insoluble in water and alkali. It is readily ionized by electrolysis and has a particular affinity for sulfur and halogen elements. In nature, silver is found in the elemental state and combined in ores such as argentite (Ag_2S), horn silver (AgCl), proustite (Ag_3AsS_3), and pyrargyrite (Ag_3SbS_3).

From these ores, silver ions may be leached into ground waters and surface waters, but since many silver salts such as the chloride, sulfide, phosphate, and arsenate are insoluble, silver ions do not usually occur in significant concentration in natural waters.

Silver is used extensively in electroplating, photographic supplies manufacture, electrical equipment manufacture, soldering and brazing, and battery manufacture. Of these, the two major sources of silver wastes are the photographic and electroplating industries with about 30 percent of U.S. industrial consumption of silver going into the photographic industry. Silver is also used in its basic metal state for such items as jewelry and electrical contacts.

Silver compounds can be absorbed in the circulatory system and reduced silver deposited in the various tissues of the body. A condition known as argyria, a permanent greyish pigmentation of the skin and mucous membranes, can result. Concentrations in the range of 0.4-1 mg/l have caused pathologic changes in the kidneys, liver and spleen of rats.

Silver is recognized as a bactericide, and doses as low as 0.000001 to 0.5 mg/l have been reported as sufficient to sterilize water.

Sulfates

Sulfates occur naturally in waters, particularly in the western United States, as a result of leachings from gypsum and other common materials. They also occur as the final oxidized state of sulfides, sulfites, and thiosulfates. Sulfates may also be present as the oxidized state of organic matter in the sulfur cycle, but they in turn may serve as sources of energy for sulfate splitting bacteria. Sulfates may also be discharged in numerous industrial wastes, such as those from tanneries, sulfate-pulp mills, textile mills, and other plants that use sulfates or

sulfuric acid. Thiosulfates occur in photoprocessing wastewater as part of the fix.

In moderate concentrations, sulfates are not harmful, and it has been reported that concentrations up to 1,000 mg/l are harmless. Irrigation concentrations less than 336 mg/l are considered to be good to excellent.

Because of their relatively harmless nature, sulfates are not selected as a pollutant parameter requiring the establishment of a limitation.

Oxygen Demand (BOD, COD, and TOC)

Oxygen Demand

Organic and some inorganic compounds can cause an oxygen demand to be exerted in a receiving body of water. Indigenous microorganisms utilize the organic wastes as an energy source and oxidize the organic matter. In doing so their natural respiratory activity will utilize the dissolved oxygen.

Dissolved oxygen (DO) in water is a quality that, in appropriate concentrations, is essential not only to keep organisms living but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at reduced DO concentrations that makes them less competitive and less able to sustain their species within the aquatic environment. For example, reduced DO concentrations have been shown to interfere with fish population through delayed hatching of eggs, reduced size and vigor of embryos, production of deformities in young, interference with food digestion, acceleration of blood clotting, decreased tolerance to certain toxicants, reduced food utilization efficiency, growth rate, and maximum sustained swimming speed. Other organisms are likewise affected adversely during conditions of decreased DO. Since all aerobic aquatic organisms need a certain amount of oxygen, the consequences of total depletion of dissolved oxygen due to a high oxygen demand can kill all the inhabitants of the affected aquatic area.

It has been shown that fish may, under some natural conditions, become acclimatized to low oxygen

concentrations. Within certain limits, fish can adjust their rate of respiration to compensate for changes in the concentration of dissolved oxygen. It is generally agreed, moreover, that those species which are sluggish in movement (e.g., carp, pike, eel) can withstand lower oxygen concentrations than fish which are more lively in habit (such as trout or salmon).

The lethal effect of low concentrations of dissolved oxygen in water appears to be increased by the presence of toxic substances, such as ammonia, cyanides, zinc, lead, copper, or cresols. With so many factors influencing the effect of oxygen deficiency, it is difficult to estimate the minimum safe concentrations at which fish will be unharmed under natural conditions. Many investigations seem to indicate that a DO level of 5.0 mg/l is desirable for a good aquatic environment and higher DO levels are required for selected types of aquatic environments.

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

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

result in the death of all aerobic aquatic inhabitants in the affected area.

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

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

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

The BOD₅ test is essentially a bioassay procedure which provides an estimate of the oxygen consumed by microorganisms utilizing the degradable matter present in a waste under conditions that are representative of those that are likely to occur in nature. Standard conditions of time,

temperature, suggested microbial seed, and dilution water for the wastes have been defined and are incorporated in the standard analytical procedure. Through the use of this procedure, the oxygen demand of diverse wastes can be compared and evaluated for pollution potential and to some extent for treatability by biological treatment processes.

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

Chemical Oxygen Demand (COD)

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

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

The compounds which are more resistant to biological oxidation are becoming of greater and greater concern not only because of their slow but continuing oxygen demand on the resources of the receiving water, but also because of their potential health effects on aquatic life and humans. Many of these compounds result from industrial discharges

and some have been found to have carcinogenic, mutagenic and similar adverse effects, either singly or in combination. Concern about these compounds has increased as a result of demonstrations that their long life in receiving water - the result of a slow biochemical oxidation rate - allows them to contaminate downstream water intakes. The commonly used systems of water purification are not effective in removing these types of materials, and disinfection such as chlorination may convert them into even more hazardous materials.

Thus the COD test measures organic matter which exerts an oxygen demand and which may affect the health of the public. It is a useful analytical tool for pollution control activities. It provides a more rapid measurement of the oxygen demand and an estimate of organic compounds which are not measured in the BOD₅ test.

Total organic carbon (TOC) is measured by the catalytic conversion of organic carbon in a wastewater to carbon dioxide. Most organic chemicals have been found to be measured quantitatively by the equipment now in use. The time of analysis is short, from 5 to 10 minutes, permitting a rapid and accurate estimate of the organic carbon content of the wastewaters to be made by relatively unskilled personnel.

A TOC value does not indicate the rate at which the carbon compounds are oxidized in the natural environment. The TOC test will measure compounds that are readily biodegradable and measured by the BOD₅ test as well as those that are not. TOC analyses will include those biologically resistant organic compounds that are of concern in the environment. BOD and COD methods of analyses are based on oxygen utilization of the wastewater. The TOC analyses estimate the total carbon content of a wastewater. There is as yet no fundamental correlation of TOC to either BOD or COD. However, where organic laden wastewaters are fairly uniform, there will be a fairly constant correlation among TOC, BOD and COD. Once such a correlation is established, TOC can be used as an inexpensive test for routine process monitoring.

182

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

Thus far, the Photoprocessing Industry has been characterized with regard to processes used, water use, wastes generated, pollutants of concern, in-process control technologies used, end-of-pipe treatment technologies employed, effluent quality, and wastewater discharge destinations. This section discusses the extent to which the current use of in-process controls and end-of-pipe treatments by this industry reduces pollutant discharge. Other technologies that are either being considered or are possibly applicable for the treatment of wastewater generated by photoprocessors are also discussed.

IN-PROCESS CONTROL TECHNOLOGIES

The control technologies employed by the photoprocessing industry are described in detail in Section III of this document. These consist of process modifications to reduce discharge of expensive materials such as silver and complex cyanide salts. Although these practices are used primarily for resource recovery, their use results in a secondary benefit of reducing the pollutant load in process wastewater.

Recovery and Regeneration Processes

An estimate of the extent of use of some in-process controls and treatments currently used in the industry is shown in Table VII-1.

As shown in Table VII-1, most of the facilities in the four largest size categories recover silver and regenerate ferricyanide bleach. It is also estimated that a similar proportion of the facilities regenerate their ferric EDTA bleach and bleach-fix. Recovery of silver from wash water using ion exchange or reverse osmosis is practiced by only a relatively small number of the larger facilities. An even smaller number of facilities regenerate other solutions such as developers and prewashes. Most facilities which process

TABLE VII-1
ESTIMATED BREAKDOWN OF IN-PROCESS CONTROL AND TREATMENT USE BY PLANT SIZE (DAILY PRODUCTION)

Production sq ft/day (sq ft/day)	Production Size Category	Number of Plants	PERCENTAGE OF PLANTS USING INDICATED CONTROLS BY SIZE CATEGORY										Reduction of Wastewater by Evaporation
			Silver Recovery	Ion Exchange	Reverse Osmosis	Ferricyanide Bleach Regeneration	FeSO ₄ Precipitation	Dichromate Treatment					
<93 (<1,000)	<A	9,900	*	0	0	0	*	0	0	0	0	0	0
93-186 (1,000-2,000)	A	200	95	2	0	50	0	0	0	0	0	0	0
186-464 (2,000-5,000)	B	305	100	8	0	60	0.3	0	0	0	0	0	0
464-4,640 (5,000-50,000)	C	200	100	2	0	90	3	0	0	0	0	0	0
4,640-∞ (50,000-∞)	D	15	100	20	33	95	20	0	0	0	0	7	0

* Insufficient information to make reasonable estimate.

VII 2
184

color reversal (DC) film recover and reuse color couplers from the developers. The following sections give brief accounts of both bleach regeneration and silver recovery techniques in current use and present information on their capability of reducing wastewater loadings. Developer regeneration and coupler recovery result in potential reduction of TOC in the raw waste. For those plants processing color paper containing cadmium compounds, developer regeneration also has the potential for reduction of cadmium in the raw waste. Insufficient data are available to quantify this reduction.

Bleach Regeneration

Bleach regeneration is used in the industry to reprocess ferricyanide bleach, EDTA bleach and bleach-fixes. The environmental benefits of using these techniques are discussed below.

Tables VII-2 through VII-4 show the environmental benefits of ferricyanide bleach regeneration and summarize the combined data obtained during the study. The data presented in these tables and the succeeding tables in this section have been extracted from the data tables in Section V and grouped according to the indicated plant characteristics. Some of the plants, for which cyanide values are given in the Section V effluent data tables, are not included in Tables VII-2 through VII-4. The available information from the plants not included was insufficient to allow a determination of the particular bleach treatment category. The production normalized total cyanide values reported are based on the areas of product processed with ferricyanide bleaches. These data are plotted as a cumulative distribution in Figures VII-1 through VII-3. Cumulative distribution plots are used here to show trends or grouping of data. Sudden changes in slope or discontinuities in the data displayed in such a plot indicate that the data groups may belong to different populations.

Considerably lower total cyanide effluent levels result from the use of regeneration methods. An additional benefit results in the treatment of the waste fix by ferrous sulfate (FeSO_4) precipitation as shown in Table VII-4. It should be noted that the fix waste is treated and discharged in batches at the listed plants. The plant effluents

represented in Table VII-4 do not contain any treated waste fix batches. However, data taken from plant 4550's fix blowdown indicate that the treated waste contributes 0.9 percent of the total cyanide waste load. The processing and controls used in all plants listed in the table are comparable to 4550.

EDTA based bleach fixes are also regenerated within the industry. The benefits here are similar to those described earlier for the ferricyanide bleaches (i.e., a reduction of pollutant raw waste loading and a saving of processing raw materials).

Dichromate based bleaches are not regenerated as such in this industry. Some plants reconstitute waste dichromate bleach by discharging about 50 percent of the waste and reconstitute the remainder by chemical addition.

TABLE VII-2
Total Cyanide Content in Plant Effluent of Plants
Using Ferricyanide Bleach with No Regeneration

<u>Plant</u>	<u>Total cyanide load, kg/1,000 sq m (lb/1,000 sq ft)</u>
0201	8.3 (1.7)
0204	23 (4.8)
0205	48 (9.8)
0210	21 (4.3)
0218	13 (2.6)
0229	<u>18 (3.6)</u>

Av = 22 (4.5)

TABLE VII-3
Total Cyanide Content in Effluent of Plants
Using Ferricyanide Bleach Regeneration

<u>Plant</u>	<u>Total cyanide load, kg/1,000 sq m (lb/1,000 sq ft)</u>
0215	4.4 (0.90)
0223	7.3 (1.5)
1465	7.3 (1.5)
2714	8.3 (1.7)
6208*	0.78 (0.16)
8226*	<u>0.63 (0.13)</u>

Av = 4.8 (0.98)

* These plants are movie labs. Plant 6208 uses "replenish on demand" system for ferricyanide bleaches.

TABLE VII-4
Total Cyanide Content in Effluent of Plants Using
Ferricyanide Bleach Regeneration plus FeSO₄
Precipitation Treatment on Waste Fix

<u>Plant</u>	<u>Amount, kg/1,000 sq m (lb/1,000 sq ft)</u>
0232	1.3 (0.26)
0233	0.59 (0.12)
0234	2.6 (0.53)
0235	1.4 (0.28)
0236	0.59 (0.12)
0237	1.4 (0.28)
2465	1.0 (0.21)
2488	0.39 (0.08)
3437	0.26 (0.054)
4228	1.4 (0.28)
4550	0.54 (0.11)
4666	1.7 (0.34)
5552	1.9 (0.39)
6726	<u>0.76 (0.16)</u>

Av = 1.1 (0.23)

~~VII-5~~
187

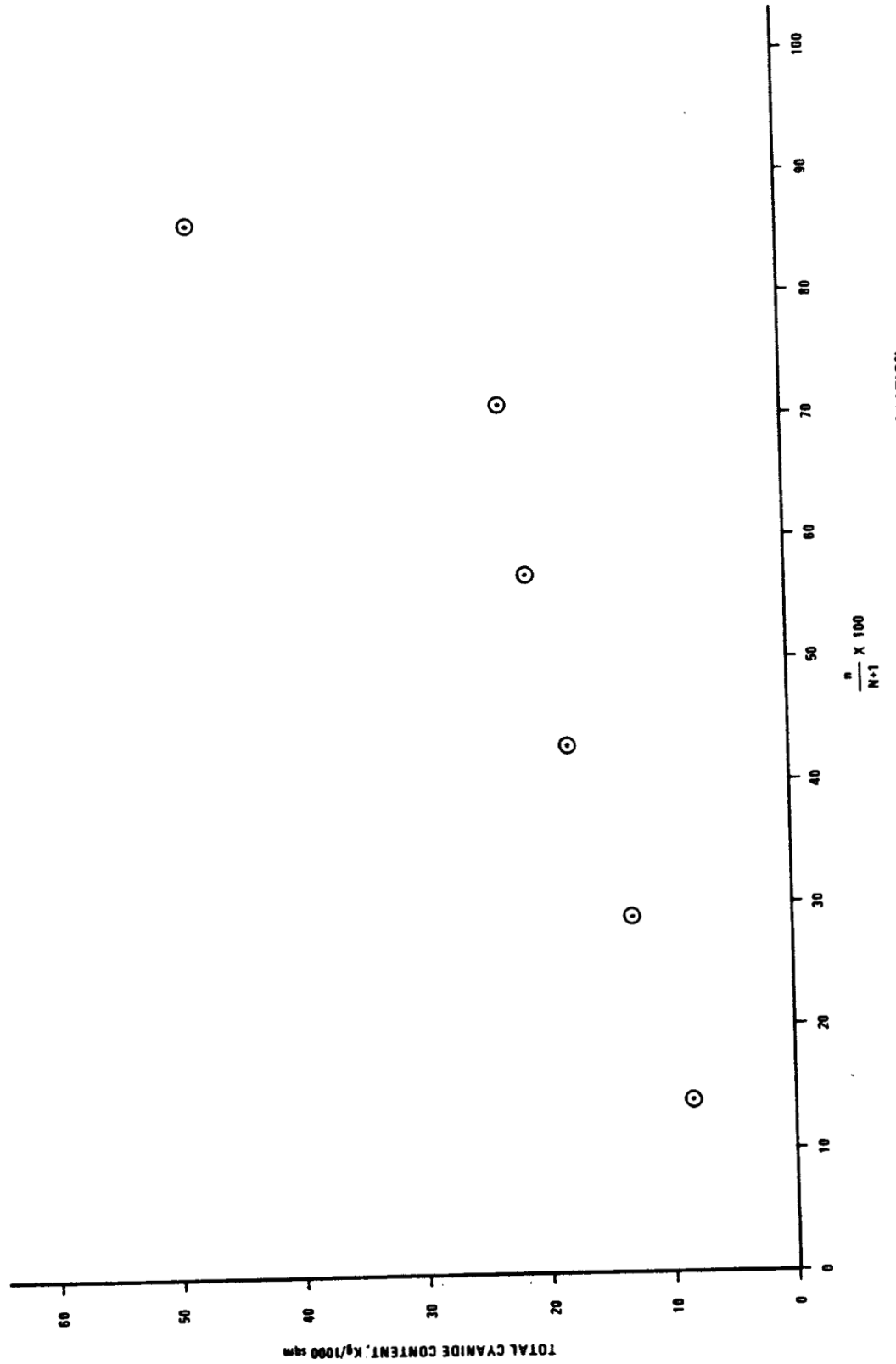


FIGURE VII-1 TOTAL CYANIDE CONTENT IN EFFLUENT - NO BLEACH REGENERATION

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881

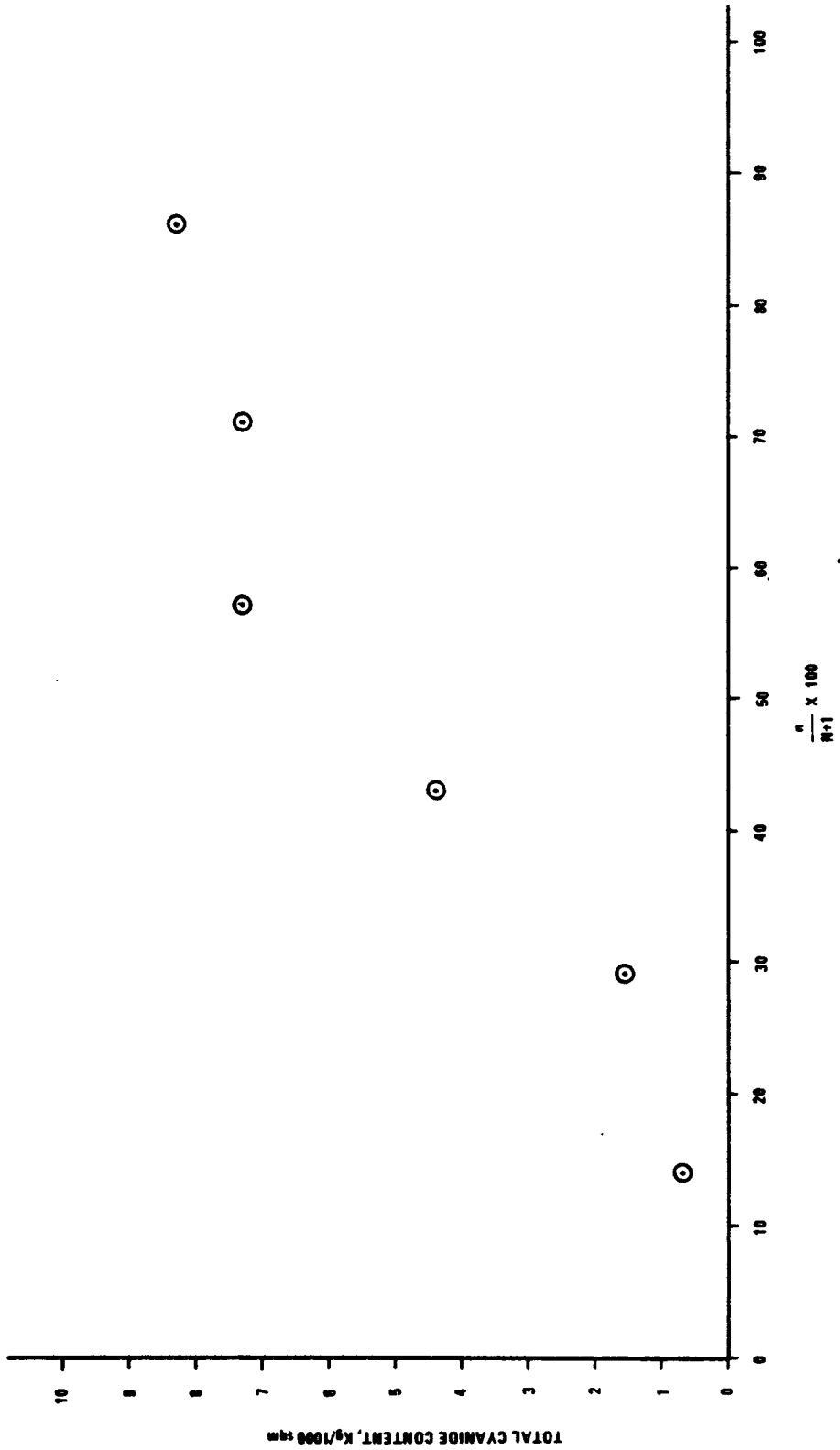


FIGURE VII-2 TOTAL CYANIDE IN EFFLUENT - PLANT USING BLEACH REGENERATION

VII-T
189

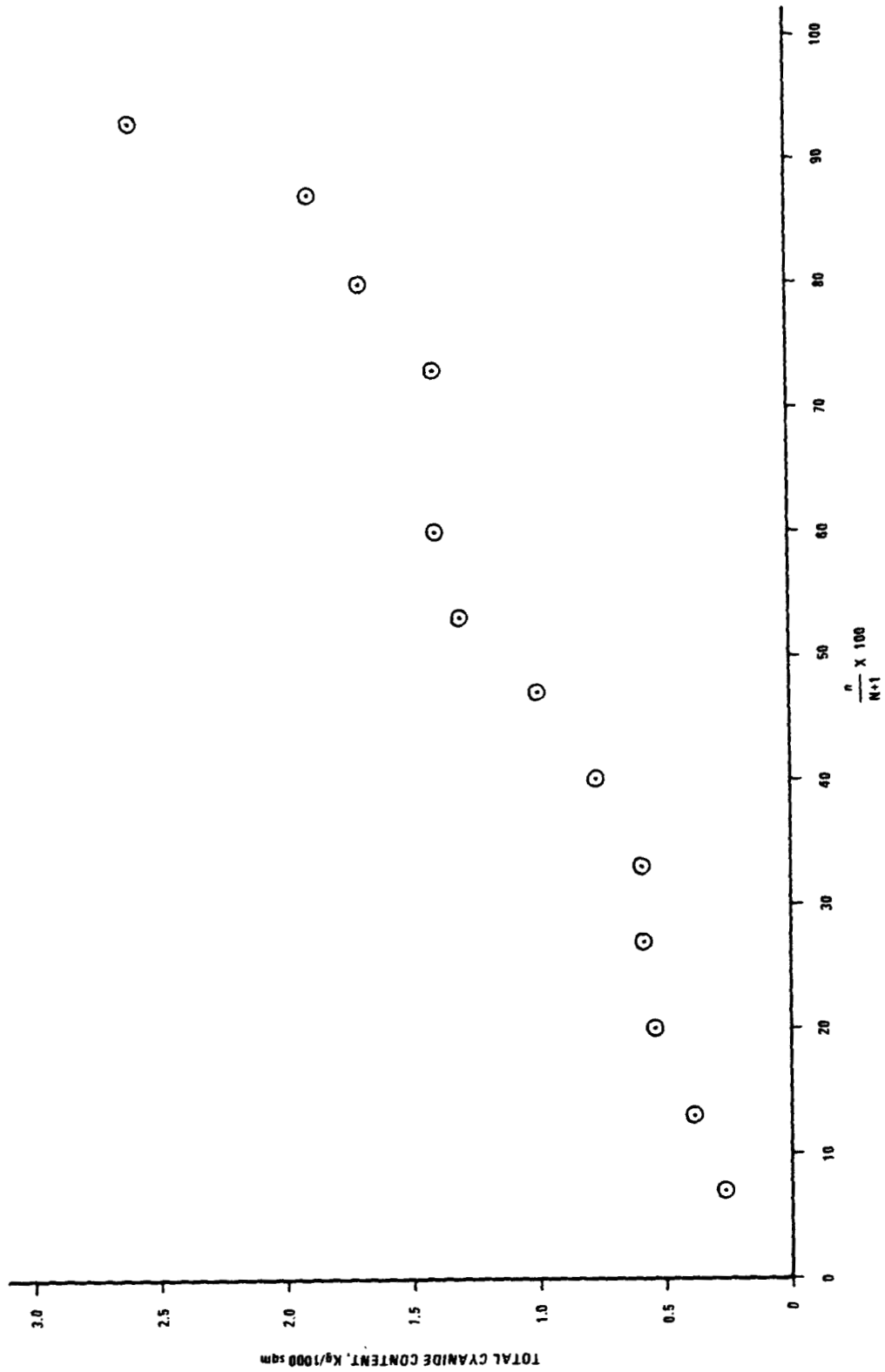


FIGURE VII-3 TOTAL CYANIDE IN EFFLUENT - BLEACH REGENERATION AND FERROUS SULFATE PRECIPITATION

VII-8
190

Silver Recovery

There are at least five methods in current use for recovery of silver from photographic processing solutions. These are metallic replacement, electrolytic plating, ion exchange, reverse osmosis, and chemical precipitation.

Tables VII-5 through VII-7 display the environmental benefits of silver recovery and summarize the information obtained. Some of the plants, for which silver values are given in the Section V effluent data tables, are not included in Tables VII-5 through VII-7. The available information from these plants was insufficient to allow a determination of the particular silver recovery category. The production normalized total silver values reported are based on the area of all material processed. These data are plotted as a cumulative distribution in Figures VII-4 through VII-6. A considerable reduction in the amount of silver in the plant effluent is achieved by the use of standard metallic replacement and electrolytic plating silver recovery processes.

The group of plants shown in Table VII-7 and Figure VII-6 either hold waste fix in holding tanks pending batch discharge or contractor haul the waste fix. As a result, the effluent samples taken from these plants contain no waste fix. The silver amount in the effluent from these plants is attributed to carryover of silver into the after-fix wash. The average quantity of silver (0.11 kg/1,000 sq m) in the effluent of the plants included in Table VII-7 supports the average silver quantity (0.14 kg/1,000 sq m) for the plants included in Table VII-6 when the relative amounts of silver in the fix after silver recovery and the wash water are considered. Although contractor hauling potentially results in reduced plant effluent silver levels, the hauled fix must be disposed of in an environmentally sound manner for this to be a net environmental benefit.

Additional reduction of discharged silver can be achieved by the use of ion exchange or reverse osmosis and chemical precipitation in addition to the standard processes as shown in Table VII-8. At present, most of the industry uses metallic replacement and electrolytic plating recovery methods. Ion exchange, reverse osmosis, and precipitation

methods are used only at a few sites and then, generally, in addition to the other methods.

TABLE VII-5
Results of Silver Recovery on Silver Content in Plant
Effluent - No Silver Recovery on Some Processes

<u>Plant</u>	<u>Total silver load, kg/1,000 sq m (lb./1,000 sq ft)</u>
0204	0.47 (0.096)
0205	1.0 (0.21)
0209	0.54 (0.11)
0218	1.4 (0.29)
0223	0.25 (0.051)
0227	0.88 (0.18)
0228	0.034 (0.007)
0229	0.83 (0.17)
0230	<u>0.78 (0.16)</u>

Av = 0.68 (0.14)

TABLE VII-6
Results of Silver Recovery on Silver Content in
Plant Effluent - Silver Recovery on All Processes

<u>Plant</u>	<u>Total silver load, kg/1,000 sq m (lb/1,000 sq ft)</u>
0201	0.12 (0.025)
0202	0.17 (0.034)
0203	0.22 (0.045)
0210	0.088 (0.018)
0211	0.17 (0.034)
0213	0.21 (0.044)
0214	0.037 (0.0075)
0220	0.054 (0.011)
0221	0.34 (0.07)
0224	0.073 (0.015)
0225	0.15 (0.031)
0226	0.23 (0.048)
0232	0.13 (0.027)
0233	0.049 (0.010)
1421	0.27 (0.055)
1465	0.13 (0.026)
2146	0.32 (0.066)
2714	0.063 (0.013)
5120	0.0013 (2.6 x 10 ⁻⁴)
8226	<u>0.054 (0.011)</u>

Av = 0.14 (0.029)

~~VII-11~~
193

TABLE VII-7
 Results of Silver Recovery on Silver Content in
 Plant Effluent - Silver Recovery on All Waste Fix
 But Waste Fix Not in Sample

<u>Plant</u>	<u>Total silver load, kg/1,000 sq m (lb/1,000 sq ft)</u>
0021	0.16 (0.032)
0206	0.059 (0.012)
0234	0.059 (0.012)
0235	0.19 (0.039)
0236	0.088 (0.018)
0237	0.14 (0.028)
0662	0.12 (0.025)
1635	0.25 (0.052)
2465	0.088 (0.018)
2488	0.10 (0.021)
3437	0.028 (0.0058)
3630	0.043 (0.0089)
4228	0.14 (0.028)
4550	0.078 (0.016)
4666	0.068 (0.014)
5552	0.059 (0.012)
6174	0.054 (0.011)
6582	0.13 (0.026)
6726	0.17 (0.034)

Av = 0.11 (0.022)

~~VII-12~~
194

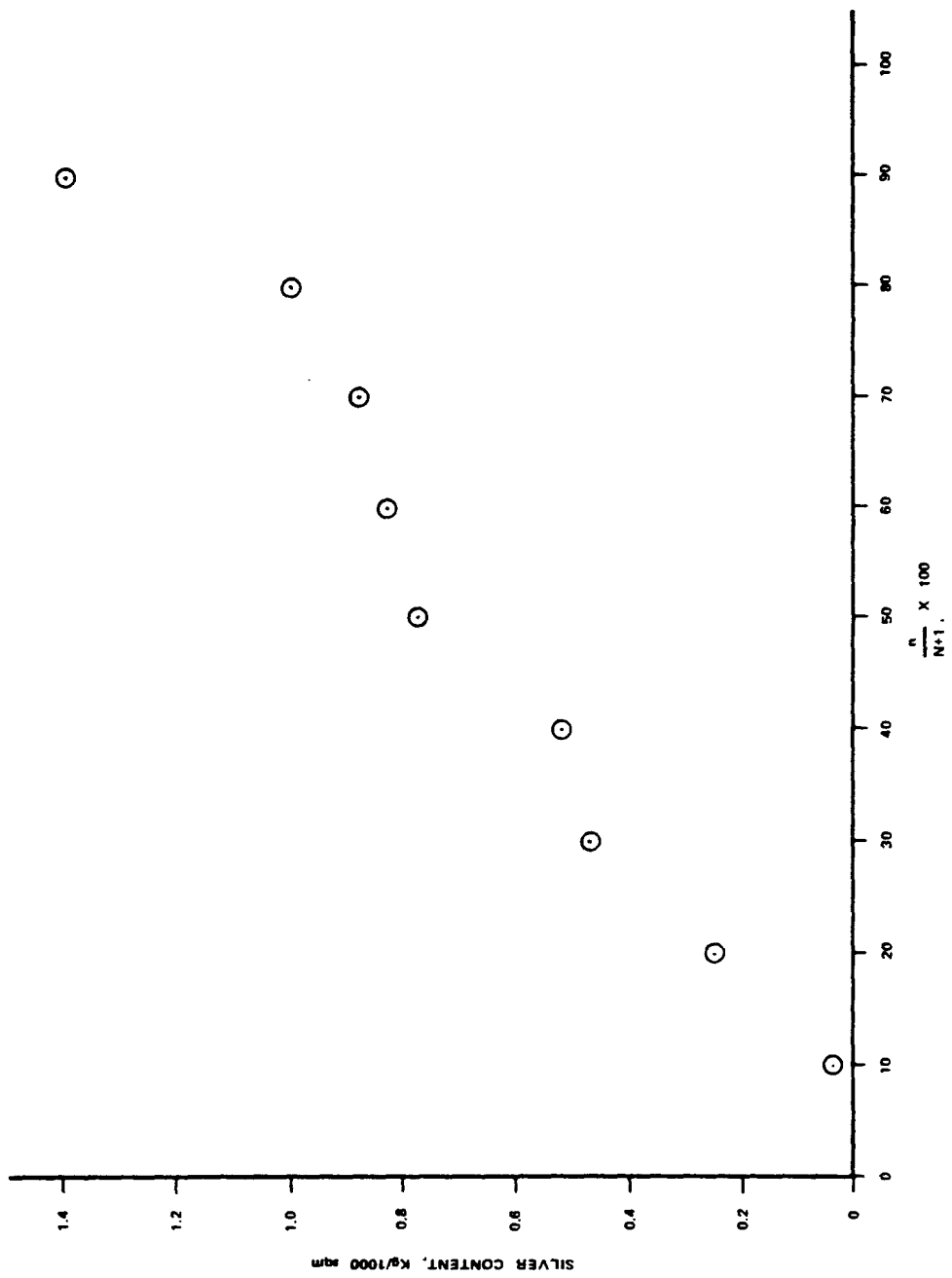


FIGURE VII-4. SILVER CONTENT IN EFFLUENT—NO SILVER RECOVERY ON SOME FIX SOLUTIONS

VII-13
195

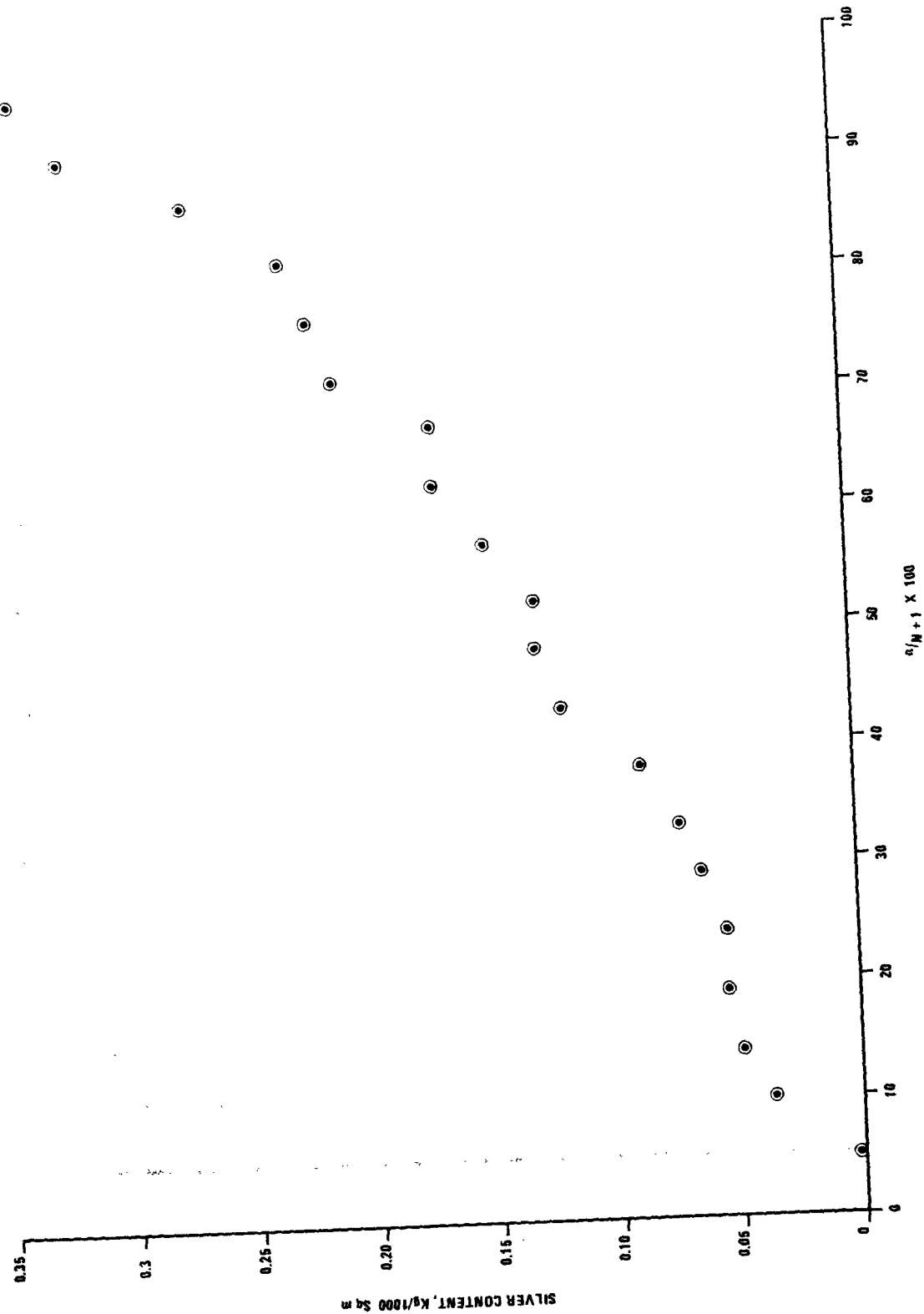


FIGURE VII-5 SILVER CONTENT IN EFFLUENT -- SILVER RECOVERY ON ALL WASTE FIX

~~VII-14~~
196

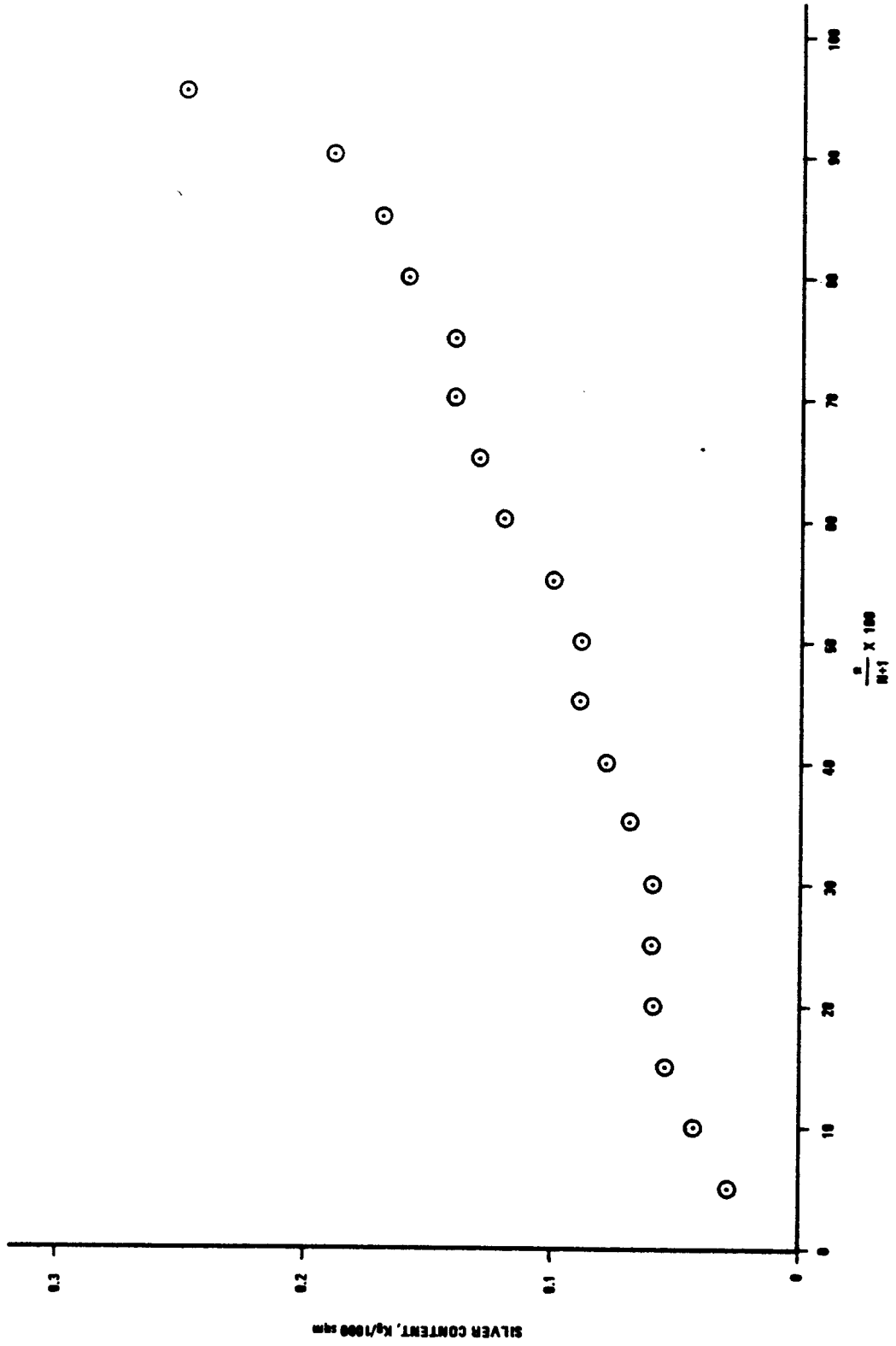


FIGURE VII-9 SILVER CONTENT IN EFFLUENT - WASTE FIX NOT IN SAMPLE

~~VII-15~~
197

TABLE VII-8
 Results of Silver Recovery on Silver Content in
 Plant Effluent - Conventional Silver Recovery on All Waste
 Fix plus Additional Recovery By:

Ion Exchange on Wash Water Plus Wash Water Recycle

<u>Plant</u>	<u>Total silver load, kg/1,000 sq m (lb/1,000 sq ft)</u>
6208	0.048 (0.0098)

Precipitation Plus Reverse Osmosis Treatment of Wash
 Water and Wash Water Recycle

7781	0.0088 (0.0018)
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Table VII-9 compares the efficiencies of individual silver recovery units used at some of the facilities. These data show the effects of specific treatments on individual wastewater streams. The operating conditions used for either the electrolytic or metallic replacement silver recovery processes will determine the efficiency of silver recovery. The efficiencies calculated for reverse osmosis are based on the incoming water versus the permeate. The concentrate solution from the reverse osmosis unit contains high concentrations of silver which should be recovered. The relative efficiencies of the various types of units are not directly comparable with each other because of the varying silver and other pollutant levels in the treated solutions.

TABLE VII-9
Effectiveness of Various Silver
Recovery Procedures

<u>Plant</u>	<u>Recovery Process</u>	<u>Concentrations of Silver Present, (mg/liter)</u>		<u>Removal Efficiency, Percent</u>
		<u>Influent</u>	<u>Effluent</u>	
6208	Ion exchange (wash water)	2.0	0.14	93
9061	Ion exchange (wash water) Unit 1	0.74	0.04	95
	Unit 2	0.60	0.10	84
4550	Metallic Replace- ment	1,580	4.7	99.7
	Electrolytic (primary plus tailing)	576	21	98
7781	Reverse Osmosis (wash water)	68	14	79
	Chemical Precipi- tation (RO concen- trate plus waste fix)	57	0.08	99.9
2714	Reverse Osmosis (paper wash)	6.3	0.04	99
	Reverse Osmosis (film wash)	0.99	<0.02	98+

The relationship between the effluent concentration and the effluent amount for silver and the percent of production using ferricyanide bleach for total cyanide is shown graphically in Figures VII-7 and VII-8, respectively. The graphs show a poor dependency between concentration and amount for silver or between concentration and production percentage for total cyanide. Therefore, a concentration

~~VII-11~~
199

based limitation would not necessarily limit the amount discharged.

A "low-flow prewash" has been used on an experimental basis at plants 3630 and 6174 to allow conventional recovery of silver from after-fix wash water. The technique as described in Section III segments the after-fix wash tank into prewash and final wash tanks. The prewash tank receives the fix dragout and has a separate fresh water input and overflow. The water input flow is optimized depending on the rate of waste fix carry-in and its silver concentration and the final silver treatment level of the prewash. The benefits of using this system, based on theoretical calculations and the results from plant 3630, are shown in Table VII-10. These calculations were made using the following assumptions:

- (1) Paper wash rate = 5.7 liters/min
- (2) Silver concentration of normal paper wash = 6.1 mg/l
- (3) Bleach-fix silver concentration = 1,900 mg/l
- (4) The carry-over flow rate from the bleach-fix to the wash is calculated to be 0.018 liters/min

Plant 3630 installed a prewash system on a color paper processor. Silver was recovered from the prewash tank overflow with a conventional metallic replacement cannister. The results obtained from this system over a period of 145 days are summarized below and in Table VII-10.

Final wash flow - 5.7 liters/min
Silver concentration in normal paper wash -
1 to 5 mg/l
Bleach-fix silver concentration - 3,000 mg/l
The carryover flow rate from the bleach-fix
to the wash is calculated to be 0.018 liters/min
Silver concentration in final wash - 3.0 ± 2.5 mg/l

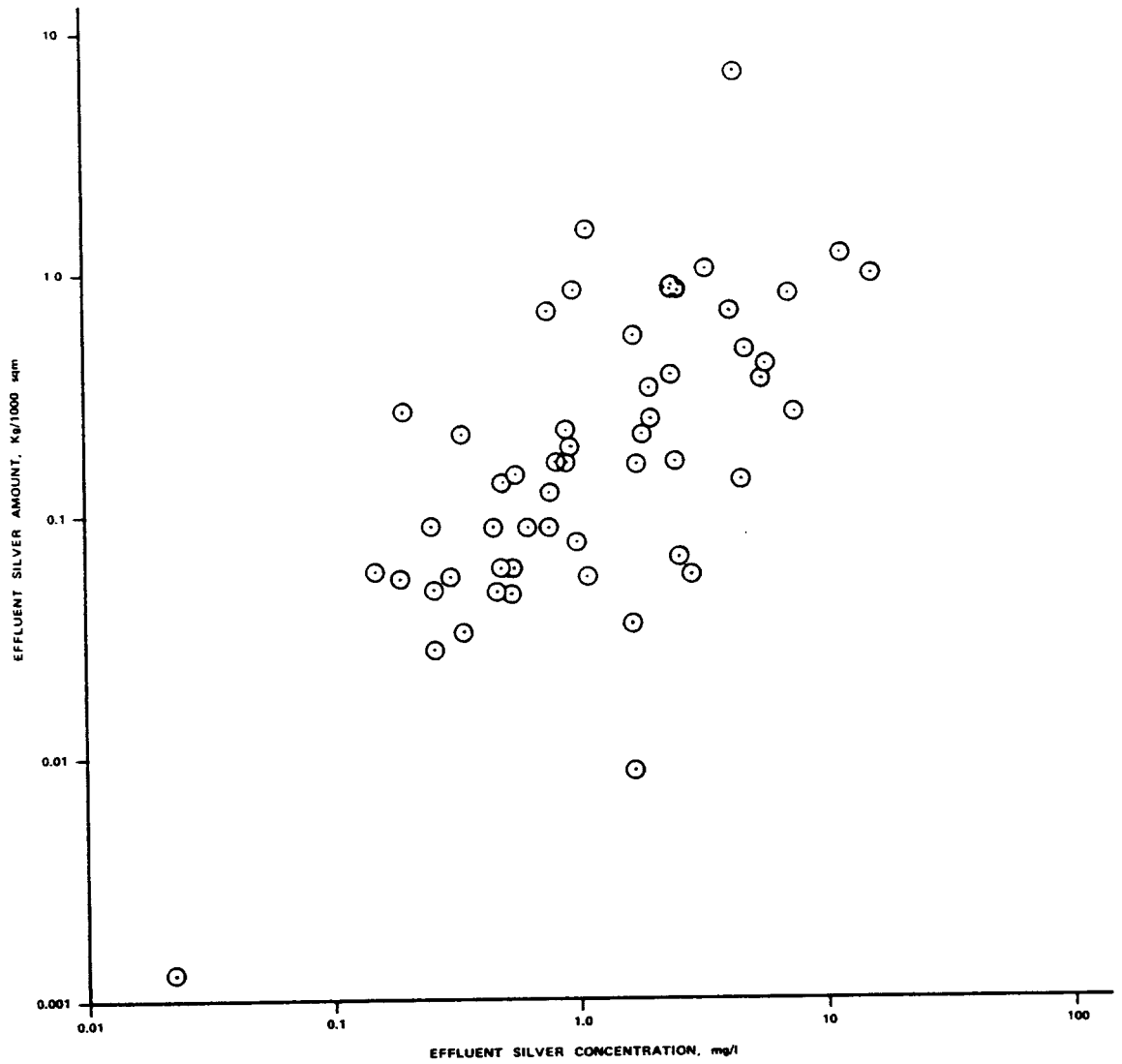


FIGURE VII-7. EFFLUENT SILVER CONCENTRATION VS EFFLUENT SILVER AMOUNT

~~VII-19~~
201

TABLE VII-10

Summary of Prewash Results

<u>CR*</u> mg/l	<u>CT**</u> mg/l	<u>Prewash Flow</u> l/min	<u>Percent Removal of Silver to Final Wash</u>	<u>Percent of Wash Water Needing Treatment</u>
Theoretical Results				
1	43.6	0.76	95.4	13.3
10	138	0.23	86.0	4.1
100	436	0.061	59.3	1.1
Experimental Results for Plant 3630				
4	200	0.10	69	1.8

*CR - Silver concentration of prewash overflow after silver recovery.

**CT - Silver concentration in prewash tank.

Plant 6174 installed an experimental prewash system on the paper processors and measured the silver concentration in the trench containing the rinse wastewater. The silver concentration of the rinse wastewater before and after installation of the prewash system averaged 2.8 mg/liter and 0.52 mg/liter, respectively.

Experimentation has shown that there are a number of potential problems in using the prewash system. These problems may be caused by trace chemical build-up, increased fix time, and improper washing. One investigator found an increase in yellow stain six months after processing and had problems with biological growth. Plants 3630 and 6174 experienced difficulties in controlling the silver recovery system on the prewash overflow and had physical quality problems introduced by required additional squeegees.

Recently a photographic supplies manufacturer, after extensive evaluation, has approved the use of a low-flow prewash on the EP-2 NR process as an alternative to the conventional wash system. The application of a prewash

system includes a recommendation for electrolytic silver recovery on the combined waste bleach-fix and prewash overflow and metallic replacement silver recovery on the electrolytic unit effluent combined with the final wash water. Suggestions for controlling biological growth in the prewash water holding tank and prewash tank are included. The recommendations include cleaning the prewash tanks with a 5 to 12 percent sodium hypochlorite solution at least weekly or more often depending upon the processing conditions.

Wash Water Recycle

Wastewater hydraulic loads can be reduced significantly by using countercurrent washing and partial recycle of wash water. The countercurrent washing referred to here involves the use of segmented wash tanks after specific chemical tanks such as bleach-fix. It does not refer to the practice of pumping the same wash water from one wash tank after a chemical tank to another wash tank after a different chemical processing solution. This could result in the intermixing of chemical solutions in the improper sequence with the process chemistry. Table VII-11 shows the results of countercurrent washing and wash water recycle for two plants. Both plants are large and a major proportion of the total production is prints made from original negatives (6208 is a movie lab and 7781 is a portrait studio). The recycled water is used only for the print processes at 6208 and is used for the print process and the final wash on the negative process at 7781.

The magnitude of the effluent hydraulic load from a photoprocessing plant is mostly determined by how the plant handles its process wash water, which is by far the largest use of water in this industry. The use of countercurrent washing and partial recycle of wash water after treatment with reverse osmosis reduces effluent hydraulic loads by over 90 percent. However, the applicability of these water-saving techniques depends on the processes used and the process and product mix at a particular plant. As discussed in Section III, potential problems such as biological growth, trace chemical build-up, and insufficient washing must be controlled to prevent short- and long-term adverse effects on product quality.

TABLE VII-11
Effect of Countercurrent Washing and Wash Water
Recycle on Effluent Hydraulic Loads

<u>Plant</u>	<u>Effluent Hydraulic Load, l/1,000 sq m (gal/1,000 sq ft)</u>	<u>Counter-current Washing Used</u>	<u>Recycle of Wash Water</u>
6208	98,000 (2,400) ¹	no	30% ²
7781	5,010 (123) ¹	yes	60% ³

¹ Average of 3 24-hour composite samples

² After ion exchange treatment

³ After reverse osmosis treatment

END-OF-PIPE TREATMENT TECHNOLOGIES

The end-of-pipe treatment technologies employed by photoprocessing plants were discussed in Section III and include precipitation, settling, ozonation, filtration, clarification, aeration, neutralization, equalization, chlorination, flocculation, and reverse osmosis. Ten of the twenty plants visited by EPA employed one or more of these treatment technologies as follows:

<u>Plant No.</u>	<u>Technologies Employed</u>
1465	ozonation (concentrated streams only)
4229	equalization, settling
3455	equalization, flocculation, precipitation, clarification, chlorination, settling, filtration
9297	equalization, aeration, ozonation, settling
2714	equalization, neutralization, reverse osmosis (wash water only)
4550	precipitation, flocculation, settling (only waste fix containing iron-cyanide complexes)
4849	chlorination (wash water only)
7781	aeration, ozonation, precipitation, settling, filtration
3075	settling
2387	settling

The effluent compositions obtained by several plants as a result of the treatments used were shown in Section V. The two facilities having the most extensive treatment systems (plants 7781 and 2714) also report the lowest effluent loadings for BOD, TDS, and other parameters. Also, the facilities having no end-of-pipe treatments (plants 2465, 4666, 5552, 4228 and 3437) report high effluent loadings of cyanides, BOD, and TDS. For some parameters, the loadings from these "no treatment" sites are as much as an order of magnitude greater than those reported for plants 7781 and 2714. Further inspection of the data shows considerable variation for a number of parameters even among plants having no end-of-pipe treatment. The reasons for these variations lie in differences in specific products processed, in water usage, and in plant operating procedures. These factors can influence the amounts of discharged materials. However, despite the variations in

waste loadings observed among plants, it is also observed that the application of end-of-pipe treatments does generally lead to reduced discharges of several pollutants.

Cadmium and chromium do not occur in all photoprocessing waste streams, and no generally applicable treatment technology was observed being used for these specific pollutants. Cadmium occurs in the color developer and bleach-fix wastes of plants using certain papers. The major manufacturer of papers of this type has indicated their intention to phase out cadmium. Chromium occurs in the processing waste streams from one color motion picture film process and some black and white reversal processes.

Plant 7781 has used ion exchange to remove cadmium from their wastewaters. The column was eluted and a concentrated cadmium solution resulted which had to be treated or disposed of by contractor hauling.

Plants using dichromate bleach can reduce the amount of chromium in their effluent by treating the plant effluent or by segregating and treating the after-bleach wash water and dichromate bleach solution wastes. The wash water and waste bleach contain a mixture of hexavalent and trivalent chromium. A waste bleach sample from plant 6208 had a hexavalent chromium concentration of 1,020 mg/liter and a total chromium concentration of 1,700 mg/liter. The plant effluent had hexavalent chromium and total chromium concentration ranges of <0.02 to 0.44 mg/liter and 2.8 to 3.5 mg/liter, respectively, indicating that most of the hexavalent chromium was reduced to the trivalent form in the mixed waste effluent.

Treatment of the total effluent to reduce the amount of chromium would consist of pH adjustment for precipitation of the trivalent chromium and clarification. Subsequent filtration would reduce the chromium to lower levels. The filter cake containing the precipitated chromium salts would be disposed of by contractor hauling for landfilling or equivalent disposal method.

An alternative method would be to mix the segregated after-bleach wash and bleach solution wastes and treat the relatively low volume mixture. The treatment would consist of hexavalent chromium reduction, pH adjustment for

precipitation and diatomaceous earth filtration. This technology has been successfully demonstrated by the electroplating industry for treatment of chromium. Chromium reduction efficiencies of 95 percent were achieved in waste streams having up to 525 mg/liter chromium. After-bleach wash water contains up to 100 mg/liter chromium and the waste bleach approximately 1,700 mg/liter. The mixed waste solution would have a chromium concentration of about 115 mg/liter based on the relative flows of 20 liters/hr and 2,300 liters/hr of waste bleach and wash water, respectively. Thus, the photographic wastes are within the chromium concentration range successfully treated in the electroplating industry.

Plant 6208 has, on an experimental basis, demonstrated that further volume reduction of wastewater containing chromium can be achieved by treating the wash water with an ion-exchange resin. Chromium was concentrated in the relatively low volume elutriant from the column and the wash water was recycled. The elutriant could be treated using the technology described above. The demonstration unit at 6208 removed chromium from the wash water with an average efficiency of 92 percent during normal operation.

During the later part of this study, plant 7781 completed the installation of a system which reduces the discharge of process wastewater to a minimum. (All hydraulic load and in-plant and effluent data reported in Sections V and VII for 7781 result from the in-process control and treatment system which was in place prior to the modified system that is described below. The characteristics of the before-modification system were also described in Sections V and VII.) The system, shown schematically in Figure VII-9, consists of conventional and advanced in-process controls to reduce the production of wastewater and three stages of wastewater evaporation. In-process controls used on the film process include prebath recycle, EDTA bleach regeneration, and continuous silver recovery from the fix solution. The paper process controls are: developer regeneration by ion exchange and chemical addition, bleach-fix regeneration after electrolytic silver recovery, 50 percent stabilizer recycle by chemical addition, and countercurrent after-fix washing to reduce wash water volume. All film wash water, except the after-prebath wash, and the paper wash water are collected and treated with two

reverse osmosis units. The permeate is recycled to the process. The concentrate is combined with the waste film developer, stop, and all other waste solutions and directed to the two-stage evaporator. At this point the waste contains about 2 percent solids. The first stage of the evaporator increases the solids concentration to about 20 percent and the second stage to about 65 percent. This wastewater is then pumped to the film wipe evaporator which increases the solids content of the waste to about 80 percent. The solid waste is sent to a smelter for silver reclamation. The condensate from both evaporators is condensed and passed through an ion exchange unit for reduction of ammonia. The condensed water is recycled to the process and the elutriant containing ammonia is used as lawn fertilizer or disposed of by contractor hauling. The plant has experienced mechanical difficulties with the wipe-film evaporator which require periodic repair maintenance. During these repair periods, the evaporator is shut down and the 65 percent solids content wastewater from the two-stage evaporator is contractor hauled.

VARIABILITY FACTOR

Even plants which are achieving state-of-the-art pollutant reduction occasionally experience days of above average pollutant discharge. These high days may reflect temporary imbalances in the treatment system caused by fluctuations in flow, in raw waste loading, in chemical feed, or in mixing flows within the tanks. Allowance for the random variability of the discharge of a well designed and operated plant may be made by applying a "variability factor" to the expected long-term average. The expected long-term average is then multiplied by the variability factor.

The formulation of appropriate variability factors given below is based upon observed discharge data from operating plants. The daily maximum and the 30-day average maximum variability factors, at the 99 percent confidence level, were calculated using the following relationships:

Daily maximum variability factor = $e \exp [2.326 SY - 0.5 (SY)^2]$
Where SY = standard deviation of the natural logarithms of
the measured concentrations

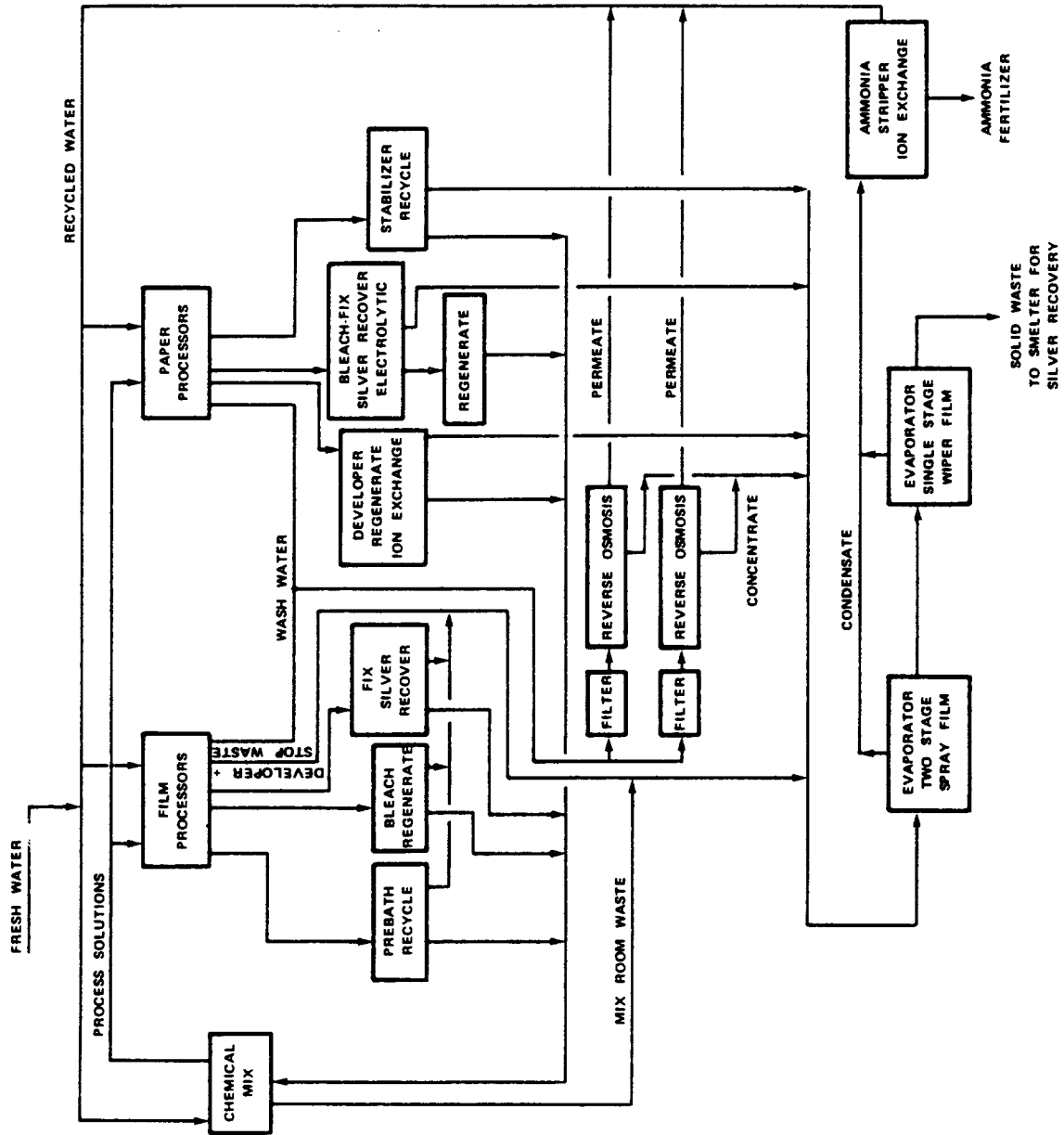


FIGURE VII-9. PROCESS WATER ELIMINATION SCHEMATIC

30-day average maximum = $[\text{mean } X + 2.326 \text{ SX}/\text{sq rt } 30]/\text{mean } X$
Where X = measured concentration
SX = standard deviation of the measured concentrations

The results of this analysis on the available long-term data are shown in Table VII-12. These data supplied by plants 6208 and 7781 are concentration values obtained from daily samples of effluent over various time periods. The raw data are given in Appendix B. A cumulative distribution plot of the silver data from plant 6208 is shown in Figure VII-10.

TABLE VII-12
POLLUTANT VARIABILITY FACTORS

Parameter	Plant	Control	Number of Values	Mean, mg/liter		Standard Deviation		30-day Average Maximum Variability Factor	Single Day Maximum Variability Factor
				X	Y	SX	SY		
Silver	6208	Ion Exchange	57	0.46	-1.1	0.37	0.96	1.3	5.9
Silver	7781	Ion Exchange	42	6.2	1.7	3.4	0.57	1.2	3.2
Silver	7781	Precipitation	20	4.0	1.2	2.5	0.64	1.3	3.6
							Silver Average	1.3	4.2
Total Cyanide	6208	Regeneration	56	0.12	-4.0	0.36	1.7	2.2	12
Chromium	6208	None	57	3.4	1.0	1.9	0.82	1.2	4.8
Cadmium	7781	Ion Exchange	64	1.2	-0.16	0.91	0.81	1.3	4.7
Cadmium	7781	Precipitation	20	0.12	-2.4	0.069	0.72	1.2	4.1
							Cadmium Average	1.3	4.4
Total Cyanide	Table VII-4	Regeneration, Precipitation	14	5.1	1.5	2.5	0.66	1.2	3.7

2/2
VII-30

$$\text{Mean } X = \frac{X_1 + X_2 + \dots + X_n}{n}$$

$$\text{Mean } Y = \frac{Y_1 + Y_2 + \dots + Y_n}{n}$$

X = measured value, mg/liter

Where $Y_1 = \ln X_1$

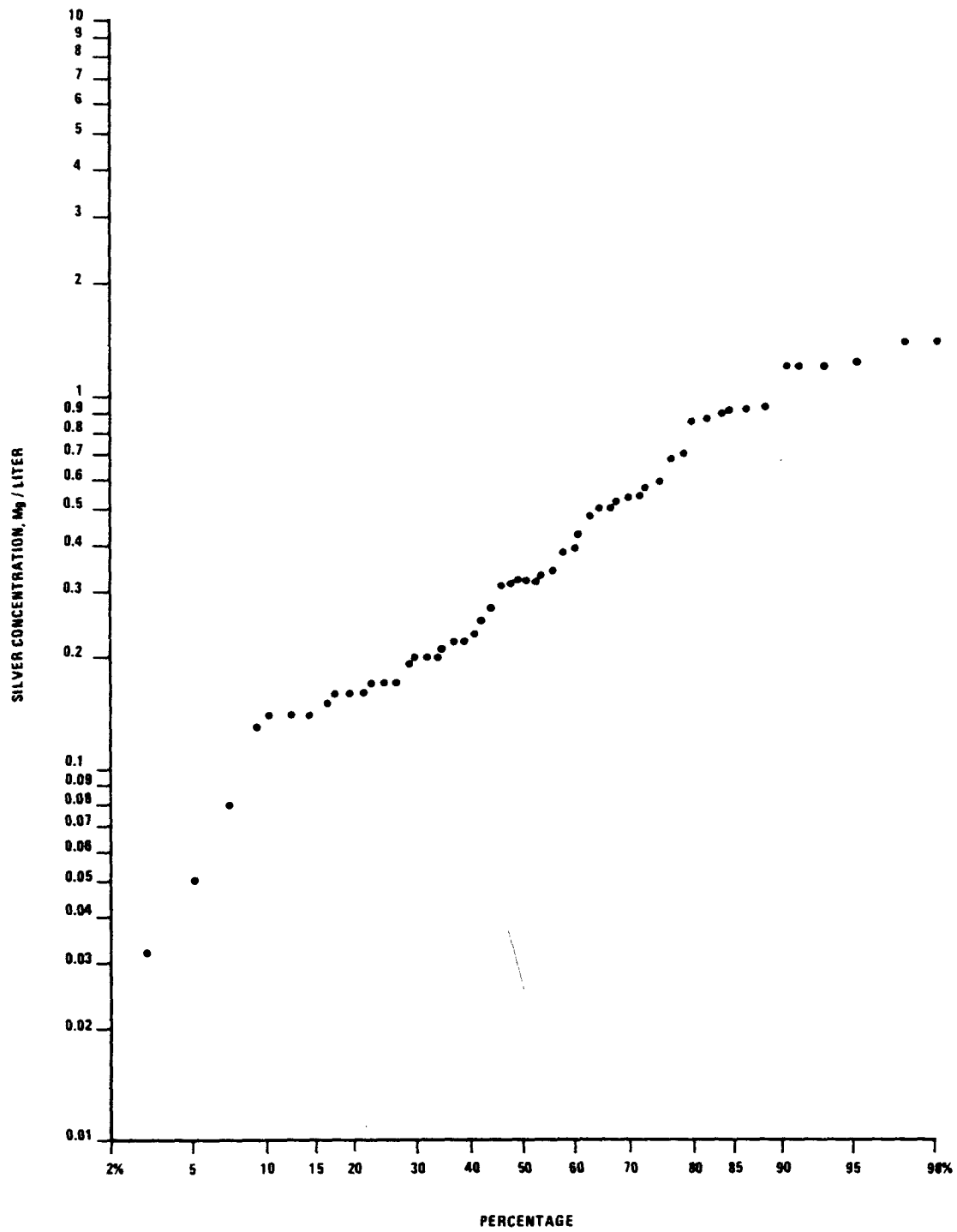


FIGURE VII-10 LONG-TERM SILVER CONCENTRATION IN EFFLUENT AT PLANT 6208

VII-31
213

214

SECTION VIII

COST, ENERGY, WASTE REDUCTION BENEFITS AND NON-WATER ASPECTS OF TREATMENT AND CONTROL TECHNOLOGIES

INTRODUCTION

Costs for the treatment and control of waterborne pollutants in the photoprocessing industry have been developed for various levels of technology currently in use in the industry. These technologies were described in Section III and their effectiveness was discussed in Section VII.

In developing the costs for the various levels of technologies, factors such as plant age, space requirements, and geographic location were considered. Age may indirectly influence control and treatment costs through the effects of isolation and control of wastes and space limitations. It was found that age was not a major cost contributing factor in this industry. The control and isolation of wastes are not generally a problem regardless of plant age because, by the nature of the photographic processing equipment and operation, wastes can be isolated. It is also observed that space limitations are not generally a problem because the control equipment is relatively compact and self-contained.

Geographic location does not significantly affect the costs of control and treatment technologies in this industry because processes used are the same throughout the United States, irrespective of geography or climate.

GENERAL COST REFERENCES AND RATIONALE

Cost information contained in this report was obtained from industry, engineering firms, equipment suppliers, and published literature. Whenever possible, costs were taken from actual installations, engineering estimates for projected facilities as supplied by contributing companies, or from equipment suppliers' quoted prices. In the absence of such information, cost estimates were developed from actual costs incurred in other industries for treatment of similar wastes. Such cost estimates were developed for the treatment of dichromate bleach wastes by using cost

~~VIII-1~~
215

information from the electroplating point source category for the treatment of chromium-containing wastes.

Interest Costs and Equity Financing Charges

Estimates for this study were based on 15 percent cost of capital, representing an overall average for either interest paid or return on investment required.

Time Basis for Costs

All cost estimates are based on 1977 prices and when necessary have been adjusted to this basis using the Chemical Engineering facility cost index.

Useful Service Life

The useful service life of treatment and control equipment varies depending on the nature of the equipment and process involved, its use pattern, maintenance and numerous other factors. Individual companies may apply service lives based on their actual experience for internal amortization. Internal Revenue Service provides guidelines for tax purposes which are intended to approximate average experience. Based on industry practice and condensed IRS guideline information, a 10-year useful service life value for control and treatment equipment was used.

Depreciation

The economic value of treatment and control equipment and facilities decreases over its service life. At the end of the useful life, it is usually assumed that the salvage or recovery value becomes zero. For IRS tax purposes or internal depreciation provisions, straight line, or accelerated write-off schedules may be used. Straight line depreciation was used solely in this report.

Capital Investment

Capital investment is defined as all front-end, out-of-pocket expenditures for providing treatment or control facilities. These costs include costs for research and development necessary to establish the process, equipment, construction and installation, services,

engineering, special start-up costs and contractor profits and contingencies.

Annual Capital Costs

Most, if not all, of the capital costs are accrued during the procurement and installation of the equipment. This present worth sum can be converted to equivalent uniform annual disbursements by utilizing the Capital Recovery Factor Method:

$$\text{Uniform Annual Disbursement} = \frac{P i (1 + i)^n}{[(1 + i)^n - 1]}$$

Where P = present value (capital expenditures),

i = interest rate, %/100

n = useful life in years

Using an interest cost of 15 percent and a useful life of 10 years:

$$\begin{aligned} \text{Uniform Annual Disbursement} &= \frac{0.15 P (1.15)^{10}}{[(1.15)^{10} - 1]} \\ &= 0.199 P \end{aligned}$$

Land Costs

Land costs are not a significant factor affecting control and treatment costs in this industry, since the equipment is generally compact and self-contained and can be housed in existing facilities. Interior space costs were not considered.

Operating Expenses

Annual costs of operating the treatment or control facilities include labor, supervision, materials, maintenance, taxes, and insurance. Power and energy costs were estimated by determining the electrical requirements for the equipment and using five cents per kilowatt-hour for the cost of electrical energy. Operating costs combined with annualized capital costs give the total annual costs

for treatment and control. The total annual operating costs minus the return from recovered silver and chemical cost savings represent the net annual operating costs. No interest cost was included for operating (working) capital. Since working capital might be assumed to be one-sixth to one-third of annual operating costs (excluding depreciation), about 1-2 percent of total operating costs might be involved. This is considered to be well within the accuracy of the estimates.

It is recognized that all costs and cost benefits for conventional silver recovery and bleach regeneration are costs incurred as a result of normal industry business practice based on economic rather than environmental incentives. As was shown in Table VII-1, most of the industry use these in-process controls. Costs for these controls are included in this section for information purposes and for those few facilities that do not presently use them.

Representative Facilities

Some cost information was obtained from the plants studied and from control and treatment equipment suppliers. These cost data cover a wide range of plant sizes in terms of production. To facilitate costing, "typical" plant sizes were selected as being representative of each of four plant size categories that cover the range of available cost data. The "typical" plant production and production range for each representative category are given in Table VIII-1. Costs are developed for the "typical" plant in each category in the following subsections.

CONTROL AND TREATMENT COSTS FOR REPRESENTATIVE PHOTOPROCESSING PLANTS

Control and treatment costs were developed for various levels of technology at representative photographic processing plants. These costs were developed from actual cost information supplied by the plants studied and from cost estimates provided by control and treatment equipment suppliers. The costed control technologies are: (1) various levels of silver recovery, (2) EDTA bleach regeneration, (3) ferricyanide bleach regeneration, (4) precipitation of waste fix for ferricyanide reduction, (5) treatment of dichromate

~~VIII-4~~
2/8

TABLE VIII-1
PRODUCTION CATEGORIES

Production Size Category	Daily Production		Yearly* Production	
	Range 1,000 sq m/day (1,000 sq ft/day)	Typical 1,000 sq m/day (1,000 sq ft/day)	Range 1,000 sq m/yr (1,000 sq ft/yr)	Typical 1,000 sq m/yr (1,000 sq ft/yr)
A	0.093 - 0.19 (1.0 - 2.0)	0.14 (1.5)	23 - 46 (250 - 500)	35 (375)
B	0.19 - 0.46 (2.0 - 5.0)	0.33 (3.5)	46 - 116 (500 - 1,250)	81 (875)
C	0.46 - 4.6 (5.0 - 50)	1.4 (15)	116 - 1,160 (1,250 - 12,500)	350 (3,750)
D	4.6 - ∞ (50 - ∞)	7.0 (75)	1,160 - ∞ (12,500 - ∞)	1,740 (18,750)

* 250 production days per year

bleach waste for chromium reduction, and (6) use of conventional and advanced in-process controls and multi-stage evaporation to reduce process wastewater discharge to a minimum. Each of the technologies has been costed separately. To determine the total costs for a particular plant, the costs for the individual technologies should be summed depending on the size of the plant and particular system used.

The best fit regression line shown on all graphs in this section was determined by regression analysis. This analysis involved calculating the linear, exponential, logarithmic, and power regression lines and the coefficient of determination (r^2) which is a measure of goodness of fit. The regression fit which had the most favorable coefficient of determination was selected for use in cost determinations.

Silver Recovery

Silver recovery costs were developed for the recovery of silver from fix solutions using conventional recovery methods and for the recovery of silver from after-fix wash water using ion exchange or reverse osmosis. These costs, as determined for the various typical plant sizes, are given in Tables VIII-2 through VIII-4.

Specific Costing References and Rationale for Silver Recovery

Silver Recovery from Fix Solutions Using Conventional Methods--

Figure VIII-1 is a graph of silver recovery capital investment costs versus production which includes plant supplied actual costs and the estimated range of costs supplied by a major equipment supplier for representative plant sizes B, C, and D. All costs include installation. The cost information supplied by the individual plants includes costs for all types of conventional silver recovery equipment. The cost data supplied by the equipment supplier were based on the following assumptions for the B, C, and D representative plants:

TABLE VIII-2
 COSTS FOR RECOVERY OF SILVER FROM FIX SOLUTIONS
 USING CONVENTIONAL METHODS

Plant Size	A	B	C	D
Typical Annual Production, 1,000 sq m/year (1,000 sq ft/year)	35 (375)	81 (875)	350 (3,750)	1,740 (18,750)
1977 Dollars				
Capital Investment Required	4,500	8,600	26,400	90,700
Annual Costs:				
Capital Recovery	900	1,700	5,300	18,000
Operating and Maintenance	340	800	3,400	16,800
Energy and Power	500	500	1,200	2,300
Total	1,740	3,000	9,900	37,100
Annual Resource Recovery	19,100	44,600	191,000	956,000
Net Annual Cost (Benefit)	(17,360)	(41,600)	(181,100)	(918,900)

TABLE VIII-3
 COSTS FOR RECOVERY OF SILVER FROM AFTER-FIX
 WASH WATERS BY ION EXCHANGE

Plant Size	A	B	C	D
Typical Annual Production, 1,000 sq m/year (1,000 sq ft/year)	35 (375)	81 (875)	350 (3,750)	1,740 (18,750)
1977 Dollars				
Capital Investment Required	10,800	10,800	31,200	90,700
Annual Costs:				
Capital Recovery	2,150	2,150	6,200	18,000
Operating and Maintenance	1,900	3,130	10,100	46,100
Energy and Power	30	70	300	1,500
Total	4,080	5,350	16,600	65,600
Annual Resource Recovery	2,600	6,100	26,000	130,000
Net Annual Cost (Benefit)	1,480	(750)	(9,400)	(64,400)

TABLE VIII-4
 COSTS FOR RECOVERY OF SILVER FROM AFTER-FIX
 WASH WATERS BY REVERSE OSMOSIS AND PRECIPITATION

Plant Size	A	B	C	D
Typical Annual Production, 1,000 sq m/year (1,000 sq ft/year)	35 (375)	91 (875)	350 (3,750)	1,740 (18,750)
1977 Dollars				
Capital Investment Required	15,300	19,400	34,800	85,800
Annual Costs:				
Capital Recovery	3,000	3,900	6,900	17,100
Operating and Maintenance	5,150	6,600	16,400	61,000
Energy and Power	800	800	1,900	2,300
Total	8,950	11,300	25,200	80,400
Annual Resource Recovery	2,600	6,100	26,000	130,000
Net Annual Cost (Benefit)	6,350	5,200	(800)	(49,600)

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223

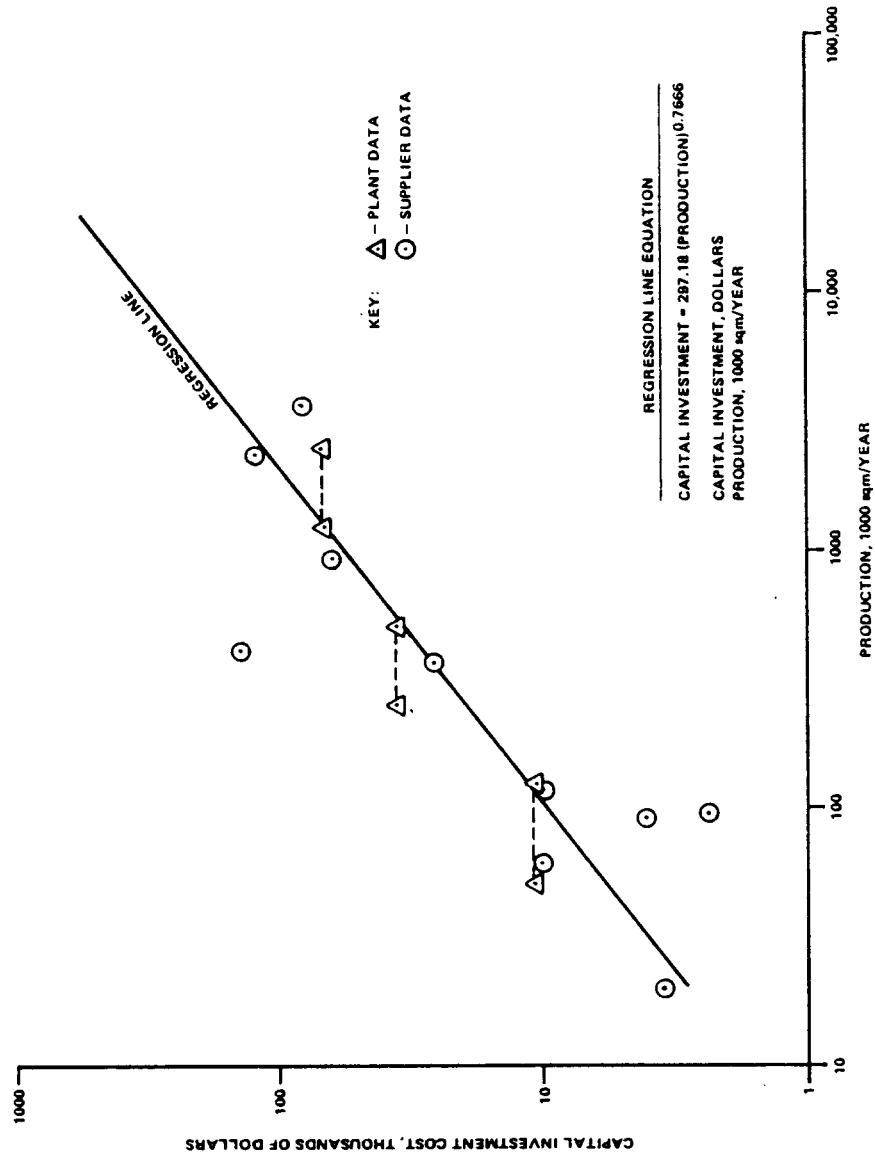


FIGURE VIII-1 SILVER RECOVERY CAPITAL INVESTMENT COSTS VS PRODUCTION

VIII-10
224

- (1) Color negative film and paper are processed with a balance of 10 percent film and 90 percent paper.
- (2) A recirculating electrolytic silver recovery system is used on the film fix with electrolytic "tailing" on fix overflow.
- (3) A batch electrolytic silver recovery system is used on the paper bleach-fix.
- (4) The B plant uses electrolytic tailing only on film fix overflow, i.e., no recirculating system.
- (5) Assumes the B and C plants have two continuous film processors and the D plant has three continuous film processors.
- (6) Installation costs are included.

The regression analysis of the data presented in Figure VIII-1 yielded the following relationship between capital investment for silver recovery equipment and production.

$$CI = 297.18(P) \exp. 0.7666$$

where:

CI = Capital investment, dollars
P = Production, 1,000 sq m/yr

This relationship was used to calculate the capital investment costs given in Table VIII-2.

Figure VIII-2 is a graph of silver recovery operating costs versus production. This curve was derived from plant supplied actual costs. The regression line is represented by the following equation:

$$OC = 9.8119(P) \exp. 0.9981$$

where:

OC = Operating cost, dollars
P = Production, 1,000 sq m/yr

~~VIII-11~~
225

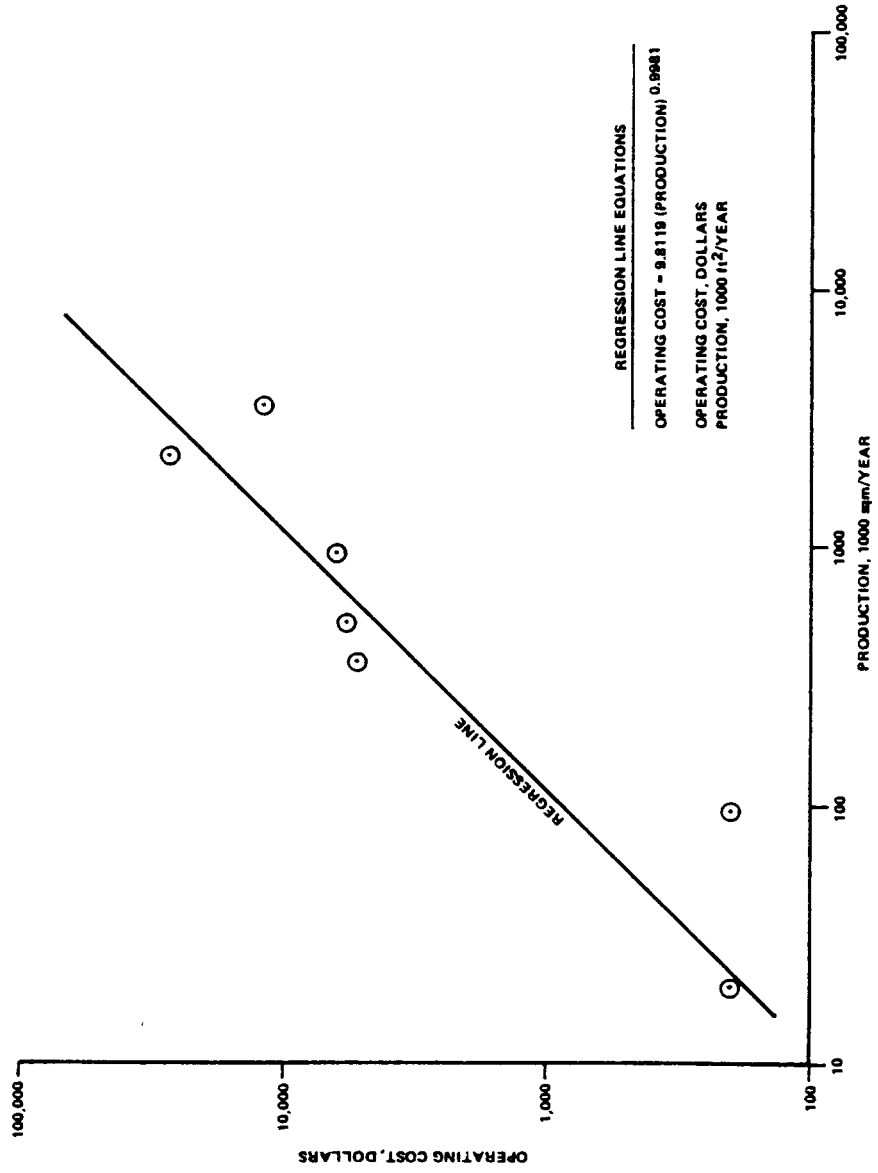


FIGURE VIII-2 SILVER RECOVERY OPERATING COSTS VS PRODUCTION

VIII-12
226

This relationship was used to calculate the operating costs in Table VIII-2.

Energy and power estimates for the representative plants were estimated from power requirements provided by the equipment supplier, an electrical energy cost of \$0.05 per kilowatt hour, and an assumed 20 hours per day, 250 days per year operation.

The annual resource recovery cost is a benefit cost that was derived from the amount of silver contained in the emulsion of the material processed by the representative plants and a silver value of \$12.00 per troy ounce. The silver recovery benefit calculation is based on the following:

- (1) A color negative plant having a 10:90 film to paper ratio.
- (2) Ninety percent of the total silver in the emulsion is contained in the fix and ten percent of the total silver is carried into the after-fix wash water.
- (3) The conventional silver recovery methods yield ninety percent of the silver contained in the fix, i.e., 81 percent of the total silver contained in the processed film and paper.

Silver Recovery from After-Fix Wash Water Using Ion Exchange--

The costs for the recovery of silver from after-fix wash water by ion exchange are given in Table VIII-3. These costs were developed using the following bases:

- (1) Information on capital and operating costs was supplied by ion exchange equipment suppliers.
- (2) The amount of equipment for each plant size is based on an estimate of the after-fix wash water flow. This estimate is based on the assumption that the after-fix wash water flow is 50 percent of the total process water hydraulic load. The average total process water hydraulic load determined for the industry is 157,000 liters/1,000 sq m (3,850 gal/1,000 sq ft) based on the data for

~~VIII-13~~
227

70 plants given in Table V-4. Therefore, the estimated after-fix wash water load is 78,500 liters/1,000 sq m (1,930 gal/1,000 sq ft).

Based on this flow estimate, the numbers of ion exchange tanks required by the various plant sizes are:

<u>Plant Size</u>	<u>Pairs of Ion Exchange Tanks</u>
A	1
B	1
C	2
D	7

- (3) Daily hours of operation for the representative plants were assumed to be 8, 8, 16, and 24 for the A, B, C, and D plants, respectively.
- (4) The maximum flow rate to each pair of ion exchange tanks is 57 liters/min (15 gal/min).
- (5) The installation costs (part of the capital investment), which include the necessary plumbing and electrical work in preparation for delivery of equipment, are estimated to be \$500 per pair of ion exchange tanks. Also included as installation costs are ten treated water analyses at \$30 each. These analyses are performed during start-up.
- (6) The ion exchange tanks are regenerated off site by the equipment supplier. The fee charged for this service is part of the operating cost. The in-plant operating and maintenance costs include maintenance labor of one hour per week per pair of tanks (labor rate at \$15,000 per year) plus one treated water analysis per regeneration at \$30 each.
- (7) The annual resource recovery cost benefit is based on the silver recovered from the after-fix wash water and waste fix. (It is assumed that the waste fix, after conventional silver recovery, is mixed with the after-fix wash water.) A total of 19 percent of the silver contained in the emulsion is

available to the ion exchange system (10 percent in the wash water plus nine percent remaining in the waste fix after conventional silver recovery). With an assumed ion exchange efficiency of 80 percent and a silver refining fee of 25 percent, the silver returned to the plant amounts to 11 percent of the silver contained in the emulsion. The annual resource recovery was computed for a 10:90 color negative film to paper ratio and with a silver value of \$12 per troy ounce.

Silver Recovery from After-Fix Wash Water Using Reverse Osmosis and Precipitation--

The costs for the recovery of silver from after-fix wash water by reverse osmosis and precipitation are given in Table VIII-4. Plant 7781 used, and supplied cost information for, a precipitation process to recover the silver from the reverse osmosis concentrate. It may be possible to use other methods to recover silver from the reverse osmosis concentrate, but no cost information was available for this specific application. Costs for the reverse osmosis and precipitation processes were developed using the following bases:

- (1) The reverse osmosis capital investment costs versus flow were provided by an equipment supplier and are shown in Figure VIII-3. The capital investment costs for the reverse osmosis equipment were derived from the following relationship:

$$CI = 9556 + 0.4016 F$$

where:

CI = Capital investment, dollars
F - Flow, 1,000 liters per day

The production of the representative plants was related to the flow by linear scaling of the input flow to a reverse osmosis unit used by plant 7781.

- (2) Reverse osmosis operating and maintenance and power costs are based on information from an equipment

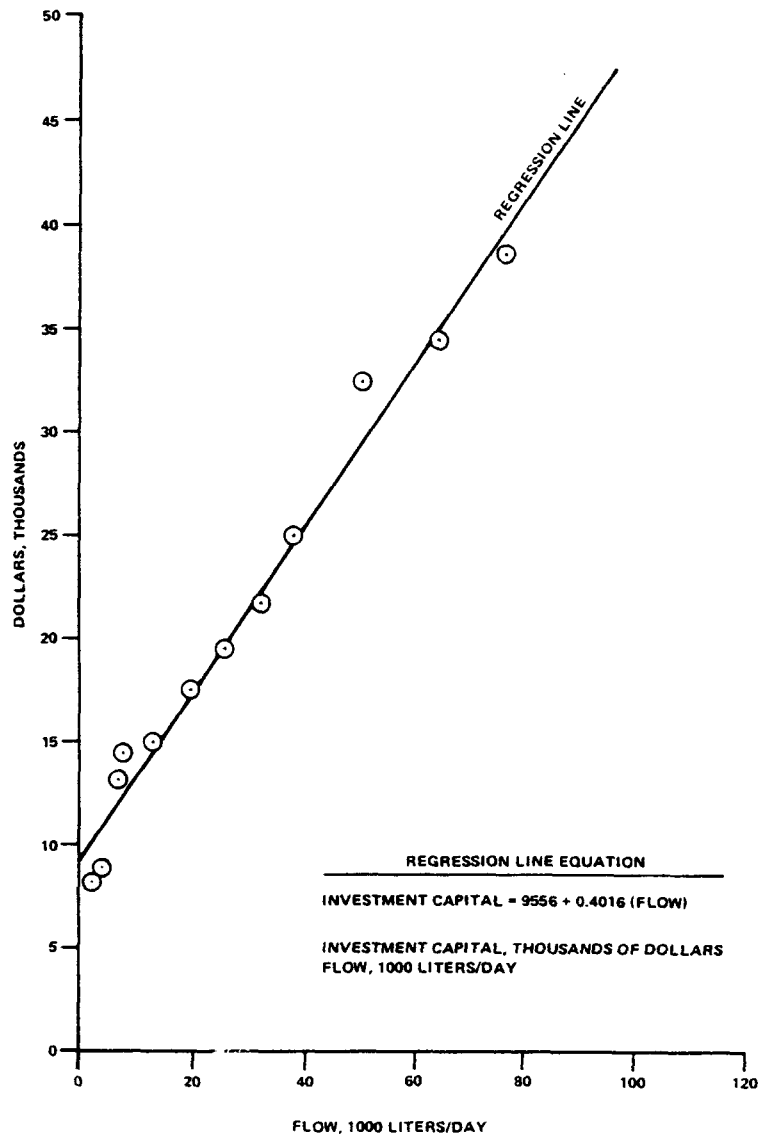


FIGURE VIII-3 REVERSE OSMOSIS EQUIPMENT CAPITAL INVESTMENT COST VS FLOW
INCLUDES REVERSE OSMOSIS, CONDUCTIVITY CONTROL AND PREFILTER

~~VIII 16~~
230

supplier. These operating and maintenance costs include membrane replacement and cleaning solution costs and labor costs for maintenance and solution analyses.

- (3) The capital investment for the precipitation of silver from the concentrate was obtained using cost information for plant 7781 and the following relationship:

$$CN = C r \exp 0.6$$

where:

CN = capital investment for representative plants, dollars
C = capital investment incurred by plant 7781, dollars
r = production ratio of representative plant to plant 7781.

- (4) Precipitation operating and maintenance and power costs were directly scaled to plant 7781.
- (5) The annual resource recovery cost benefit, as in ion exchange, is based on the silver recovered from the after-fix wash water combined with the waste fix (after conventional silver recovery). The amount of silver recovered is estimated to be the same as that determined for ion exchange.

EDTA Bleach Regeneration

The costed EDTA regeneration process consists of aeration with chemical addition. If bleach-fix is the regenerated material, it is assumed that the silver in the spent bleach-fix has been recovered by the techniques discussed in the previous section.

The collected information used to determine costs is graphically summarized in Figures VIII-4 and VIII-5. The costs, as determined for the representative plants, are shown in Table VIII-5.

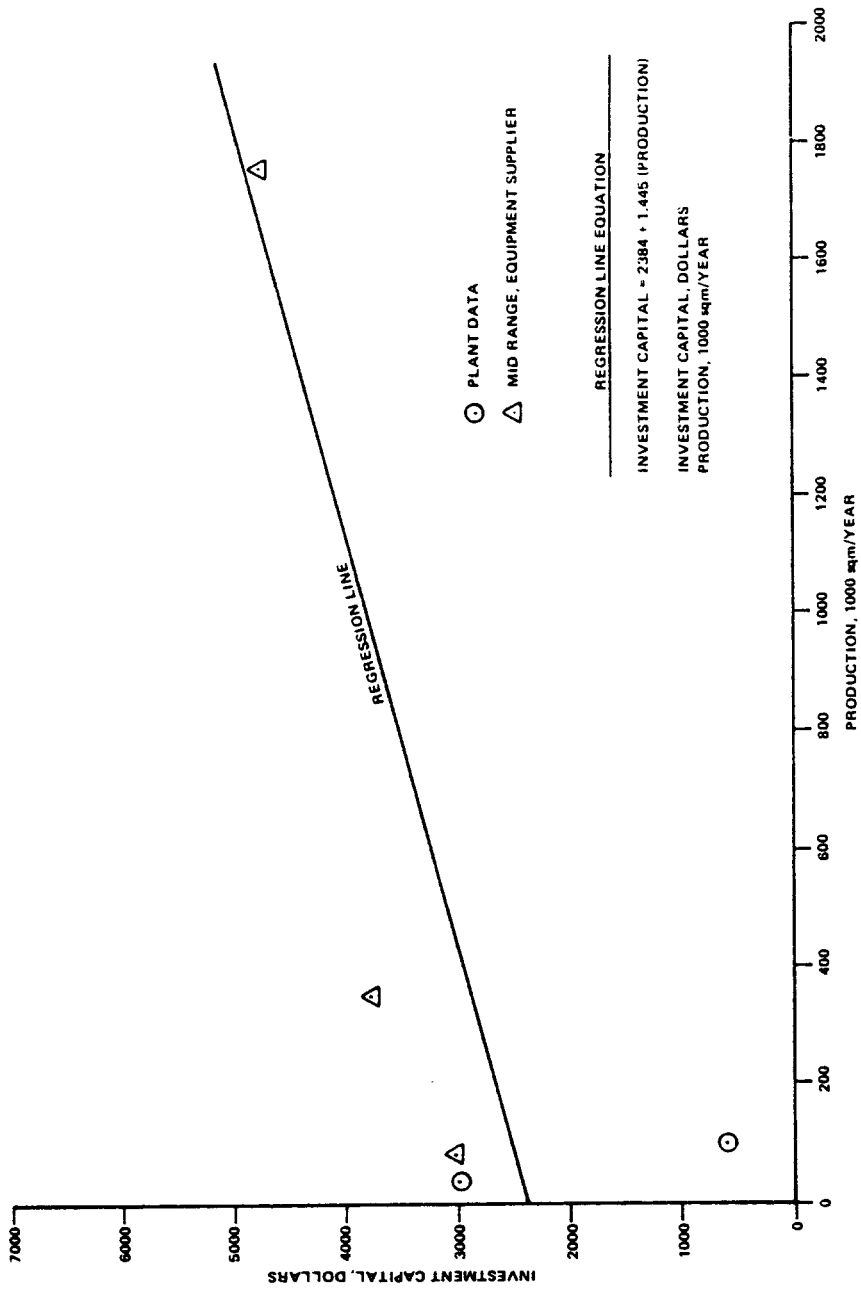


FIGURE VIII-4 Fe EDTA BLEACH REGENERATION INVESTED CAPITAL COSTS VS PRODUCTION

VIII-18
232

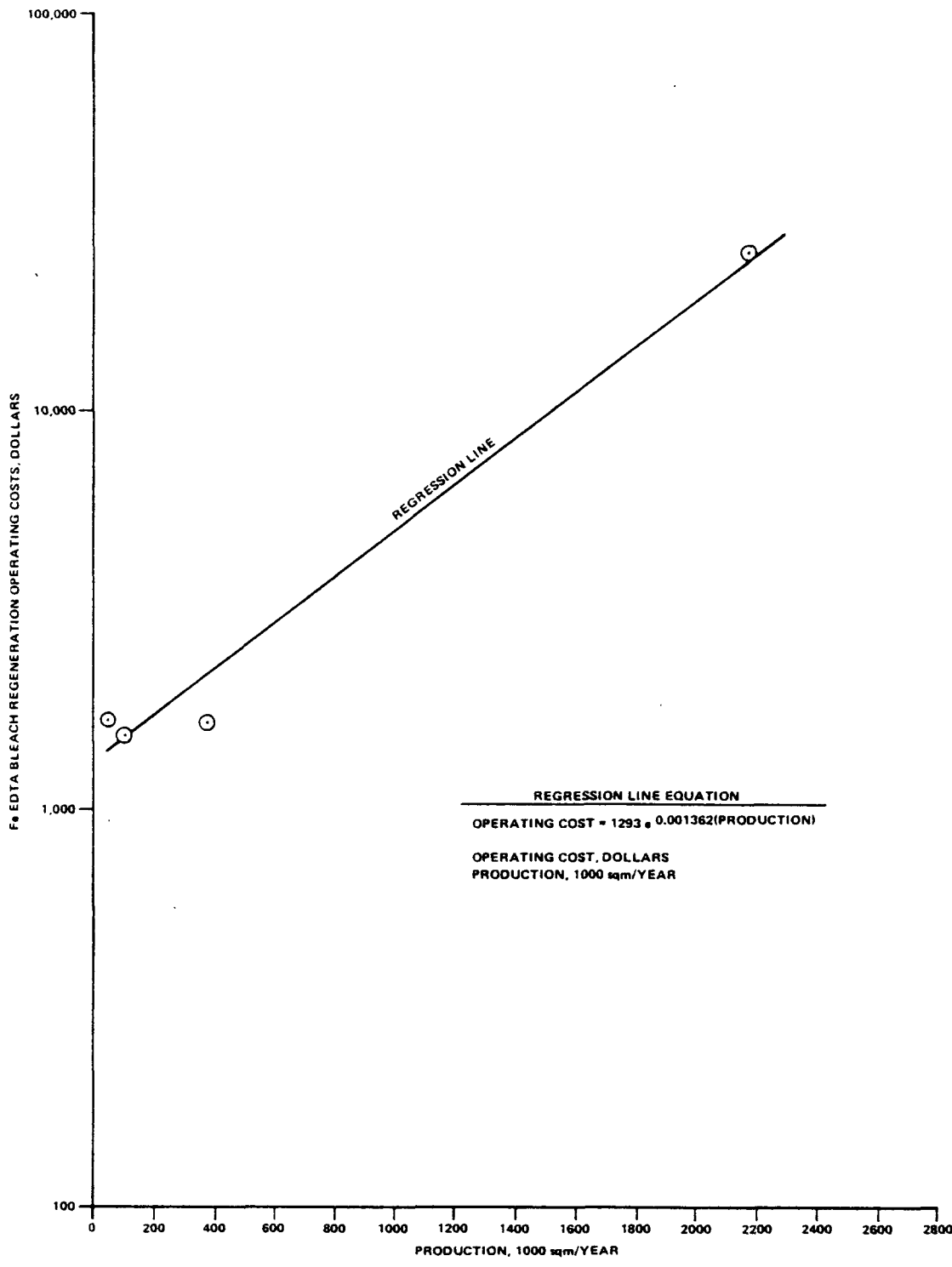


FIGURE VIII-5 F₀ EDTA BLEACH REGENERATION OPERATING COSTS VS PRODUCTION

VIII-19
233

TABLE VIII-5
 COSTS FOR FERRIC EDTA BLEACH REGENERATION BY AERATION
 AND CHEMICAL ADDITION

Plant Size	A	B	C	D
Typical Annual Production, 1,000 sq m/year (1,000 sq ft/year)	35 (375)	81 (875)	350 (3,750)	1,740 (18,750)
1977 Dollars				
Capital Investment Required	2,400	2,500	2,900	4,900
Annual Costs:				
Capital Recovery	480	500	600	1,000
Operating and Maintenance	1,360	1,400	2,100	13,800
Energy and Power	200	200	600	1,000
Total	2,040	2,100	3,300	15,800
Annual Resource Recovery	9,200	21,000	93,300	465,000
Net Annual Cost (Benefit)	(7,160)	(18,900)	(90,000)	(449,200)

VIII-20
234

Specific Costing References and Rationale for EDTA Bleach Regeneration

Figure VIII-4 is a graph of EDTA bleach regeneration capital investment costs versus production which represents plant supplied actual costs and the estimated costs supplied by a control equipment supplier for the representative plants. The costs include installation. The cost data supplied by the equipment supplier were based on the following assumptions for the representative plants:

- (1) Color negative film and paper are processed with a balance of 10 percent film and 90 percent paper.
- (2) The film process uses EDTA bleach and the paper process uses bleach-fix with a ferric EDTA base.

The following relationship between capital investment and production was derived by a regression analysis of the data presented in Figure VIII-4:

$$CI = 2384 + 1.445 P$$

where:

CI = Capital investment, dollars
P = Production, 1,000 sq m/yr

This relationship was used to calculate the capital investment costs presented in Table VIII-5.

Figure VIII-5 is a graph of EDTA bleach regeneration operating costs versus production which represents plant supplied actual costs. The following relationship between operating costs and production was derived:

$$OC = 1293 e \exp. 0.001362P$$

where:

OC = Operating cost, dollars
P = Production, 1,000 sq m/yr

The energy and power requirements were assumed to be for 1, 1, 3, and 5 horsepower motors, for the A, B, C, and D

~~VIII-21~~
235

plants, respectively, to operate air compressors for aeration. Electric energy costs were assumed to be \$0.05 per kilowatt hour with an operation time of 20 hours per day, 250 days per year.

Annual resource recovery benefits are based on the chemical savings gained by not disposing of the bleach. The determination was made, for each plant size, by taking 80 percent of the bleach chemical costs and subtracting the cost of the bleach regenerate chemicals. The following assumptions were made:

- (1) Eighty percent of the waste bleach is regenerated.
- (2) To determine bleach and bleach regenerate costs, price information for the C-41 color film and for the EP-2 color paper processes was used.
- (3) Replenishment rates of 0.925 liters/sq m (0.0227 gal/sq ft) and 0.322 liters/sq m (0.0079 gal/sq ft) were used for the C-41 bleach and the EP-2 bleach-fix, respectively.

Ferricyanide Bleach Regeneration

The costed ferricyanide bleach regeneration process utilizes ozonation for regeneration. The costs, as determined for the representative plants, are shown in Table VIII-6.

Specific Costing References and Rationale for Ferricyanide Bleach Regeneration

The specific capital investment cost information was supplied by a control equipment supplier. The equipment for the representative plants are listed below:

TABLE VIII-6
COSTS FOR FERRICYANIDE BLEACH REGENERATION BY OZONATION

Plant Size	A	B	C	D
Typical Annual Production (Film Only), 1,000 sq m/year (1,000 sq ft/year)	3.5 (37.5)	8.1 (87.5)	35 (375)	174 (1,875)
1977 Dollars				
Capital Investment Required	21,400	21,400	25,500	33,500
Annual Costs:				
Capital Recovery	4,300	4,300	5,100	6,700
Operating and Maintenance	3,400	3,400	3,400	3,400
Energy and Power	10	20	100	500
Total	7,710	7,720	8,600	10,600
Annual Resource Recovery	1,100	2,500	10,900	54,500
Net Annual Cost (Benefit)	6,610	5,220	(2,300)	(43,900)

Pollutant Parameter, kg/1,000 sq m	Effluent Without Treatment	Effluent With Treatment
Cyanide, Total	22	4.8

~~VIII-23~~
237

A and B plant - batch system

ozone generator
ozone monitor
pH control
pump
50-gallon tank

C and D plant -
continuous on-line system

ozone generator
ozone monitor
pH control
pump
100-gallon tank
automatic controls

The ozone generator was costed by selecting the nearest larger size commensurate with the plant ozone requirements based on the amount of film processed using ferricyanide bleach. The ozone requirement was related to production as stated in process specifications.

Operating costs are based on the costs given for a "typical" plant using ozone regeneration in a film processor's publication. Energy and power costs for the representative plants are based on a power requirement of 10 kwh per 0.45 kg (1 lb) of ozone generated, an ozone amount of 2.4 kg/1,000 sq m (0.48 lb/1,000 sq ft), and a power cost of \$0.05 per kwh. Annual resource recovery benefit was based on chemical savings between a plant using regeneration as compared to a plant discharging the spent bleach.

Ferrous Sulfate Precipitation of Ferricyanide

The costs established in this section are for a system to cause the precipitation of ferricyanide bleach carryover from waste fix. The costs, as determined for the representative plants, are shown in Table VIII-7.

TABLE VIII-7
 COSTS FOR FERROUS SULFATE PRECIPITATION OF FERRICYANIDE FROM WASTE FIX

Plant Size	A	B	C	D
Typical Annual Production (Film Only) 1,000 sq m/year (1,000 sq ft/year)	3.5 (37.5)	8.1 (87.5)	35 (375)	174 (1,875)
1977 Dollars				
Capital Investment Required	4,600	6,500	9,200	22,200
Annual Costs:				
Capital Recovery	920	1,300	1,830	4,400
Operating and Maintenance	600	1,220	4,490	21,400
Energy and Power	10	20	60	300
Total	1,530	2,540	6,380	26,100
Annual Resource Recovery	--	--	--	--
Net Annual Cost (Benefit)	1,530	2,540	6,380	26,100

Pollutant Parameter, kg/1,000 sq m	Effluent Without Treatment	Effluent With Treatment
Cyanide, Total	4.8	1.3

Specific Costing References and Rationale for Ferrous Sulfate Precipitation

The equipment required for ferrous sulfate precipitation of ferricyanide from waste fix is based on the equipment used by plant 4550 which includes pumps, tanks, and mixers. The equipment was sized for the representative plants according to their relative production compared to plant 4550. The capital investment was determined from individual equipment costs provided by suppliers. Related capital investment costs such as engineering, drafting, mechanical installation, and electrical work were determined from the following relationship:

$$CN = C r \exp 0.6$$

where:

- CN = capital investment for representative plant, dollars
- C = capital investment incurred by plant 4550, dollars
- r = production ratio of representative plant to plant 4550.

Operating and maintenance and power costs for the representative plants were assumed to be directly proportional to these costs for plant 4550.

Evaporation and Associated Technologies to Reduce the Discharge of Process Wastewater to a Minimum

Costs were derived for the reduction of process wastewater discharge to a minimum from information supplied by plant 7781 which is currently using the technology. The technology, using a number of techniques as described in Section VII to minimize the hydraulic load, utilizes multi-stage evaporation to reduce wastewater discharge. The costs, as determined for representative plants, are shown in Table VIII-8.

TABLE VIII-8
 COSTS FOR REDUCTION OF PROCESS WASTEWATER TO A MINIMUM
 BY ADVANCED CONTROLS PLUS MULTI-STATE EVAPORATION

Plant Size	A	B	C	D
Typical Annual Production, 1,000 sq m/year (1,000 sq ft/year)	35 (375)	81 (875)	350 (3,750)	1,740 (18,750)
1977 Dollars				
Capital Investment Required	103,000	155,000	239,000	406,000
Annual Costs:				
Capital Recovery	20,500	30,800	47,600	80,800
Operating and Maintenance	21,000	21,000	43,100	74,700
Energy and Power	400	400	1,800	8,700
Total	41,900	52,200	92,500	164,200
Annual Resource Recovery	4,200	9,900	42,400	212,000
Net Annual Cost (Benefit)	37,700	42,300	50,100	(47,800)

Specific Costing References and Rationale for the Reduction of Process Wastewater to a Minimum

Specific capital investment, operating, energy and power and annual resource recovery benefit costs were supplied by plant 7781. The information included costs for reverse osmosis treatment of wash water, developer regeneration by ion exchange, evaporation, and the reduction of ammonia in the condensate.

The capital investment costs were estimated by plant 7781 for the representative plants. Costs for special analytical equipment required for process control are included. The equipment includes a spectrophotometer and an atomic adsorption spectrometer.

The remainder of the costs for the representative plants were derived by linear scaling of the actual costs incurred by plant 7781. Labor costs for a full time analytical chemist was added to the operating costs. This cost is based on a salary of \$20,000 per annum, 3 shifts per day in the D plant, 2 shifts per day in the C plant and 1 shift per day in the A and B plants.

Treatment of Dichromate Bleach Wastes

Treatment technologies, along with the associated costs, have been established for the electroplating industry for reduction of the quantity of chromium in wastewater. The technology includes the chemical reduction of hexavalent chromium, pH adjustment for chromium precipitation, and diatomaceous earth filtration. It is recommended that these technologies be applied to after-dichromate bleach wash water mixed with the bleach overflow.

The costs are given in Tables VIII-9 through VIII-12. These costs were available in terms of flow. Film production levels comparable to these flows are included in the tables. This determination is based on an after-bleach wash water flow of 38 liters per minute (10 gallons per minute) and a film processing rate of 173 square meters per hour (1,865 square feet per hour).

TABLE VIII-9
 CONTROL AND TREATMENT COSTS FOR HEXAVALENT CHROMIUM
 REDUCTION - BATCH TREATMENT

Flow, liters/hour	189	379	1,893
Annual Film Production, 1,000 sq m/year (1,000 sq ft/year)	72 (780)	140 (1,500)	720 (7,750)
1977 Dollars			
Capital Investment Required	8,493	9,535	14,405
Annual Costs:			
Capital Cost	541	608	919
Operating and Maintenance	155	295	1,415
Energy and Power	256	256	256
Depreciation	1,699	1,907	2,881
Net Annual Cost (Benefit)	2,651	3,066	5,471

~~VIII-29~~
243

TABLE VIII-10
 CONTROL AND TREATMENT COSTS FOR HEXAVALENT CHROMIUM
 REDUCTION - CONTINUOUS TREATMENT

Flow, liters/hour	3,785	7,570	18,925
Annual Film Production 1,000 sq m/year (1,000 sq ft/year)	1,400 (15,100)	2,900 (31,200)	7,200 (77,500)
1977 Dollars			
Capital Investment Required	20,416	21,538	24,003
Annual Costs:			
Capital Cost	1,303	1,374	1,531
Operating and Maintenance	1,086	1,375	2,089
Energy and Power	256	256	256
Depreciation	4,083	4,308	4,801
Net Annual Cost (Benefit)	6,728	7,313	8,677

~~VIII-30~~
244

TABLE VIII-11
CONTROL AND TREATMENT COSTS FOR pH ADJUSTMENT (CHROMIUM TREATMENT)

Flow, liters/hour	492	4,921	49,205
Annual Film Production 1,000 sq m/year (1,000 sq ft/year)	190 (2,040)	1,900 (20,400)	19,000 (204,000)
1977 Dollars			
Capital Investment Required	1,452	4,921	18,855
Annual Costs:			
Capital Cost	93	314	1,203
Operating and Maintenance	286	1,036	3,758
Energy and Power	8	79	1,503
Depreciation	290	984	3,771
Net Annual Cost (Benefit)	677	2,413	10,315

TABLE VIII-12
 CONTROL AND TREATMENT COSTS FOR DIATOMACEOUS EARTH
 FILTRATION (CHROMIUM TREATMENT)

Flow, liters/hour	189	4,731	47,313
Annual Film Production 1,000 sq m/year (1,000 sq ft/year)	72 (780)	1,800 (19,400)	18,000 (194,000)
1977 Dollars			
Capital Investment Required	8,823	27,707	62,819
Annual Costs:			
Capital Cost	563	1,768	4,008
Operating and Maintenance	3,936	6,046	29,872
Energy and Power	22	302	1,970
Depreciation	1,765	5,541	12,564
Net Annual Cost (Benefit)	6,286	13,657	48,414

NON-WATER QUALITY ASPECTS

It is important to consider the impact of each treatment process on air, noise, solid waste, and radiation pollution of the environment to recognize and avoid the potential development of an adverse environmental impact upon these other media.

None of the control or treatment technologies considered for the photoprocessing industry have any known potential for air, noise, or radiation pollution exterior to the plant. There could be possible in-plant air pollution problems from the use of ozone or improper use of sulfide precipitation compounds. Proper use and monitoring equipment will control any potential hazard to plant personnel. Ozonation generators and reverse osmosis units create high but non-hazardous noise levels in the area close to the equipment. This problem can be alleviated with proper location and enclosure of the equipment.

The major potential non-water environmental impact from this industry is the potential generation of solid wastes. Solids generated from silver recovery are not a problem because of the obvious economic recovery value of the silver. Waste sludge from the precipitation of ferrocyanide wastes presents a solid waste disposal problem. One multi-plant company processes this sludge at a central location to reclaim the ferricyanide. Plants which do not reprocess this sludge will have to dispose of the solid waste in an approved landfill or other environmentally acceptable manner. Solid wastes generated from the treatment of waste dichromate bleach have no known market. These wastes must be disposed of in an approved landfill or other environmentally acceptable manner. Solid wastes are also generated from the plant using evaporation to eliminate process water discharge. The plant reports that the silver content is high enough to make it acceptable to a smelter for silver reclamation.

248

SECTION IX

ACKNOWLEDGMENTS

The Environmental Protection Agency was aided in the preparation of this Guidance Document by Versar Inc. Versar's effort was managed by Mr. Edwin Abrams with Mr. Lawrence G. Davies serving as principal investigator.

Mr. Richard Kinch and Mr. John Newbrough of the EPA's Effluent Guidelines Division served as Project Officers during the preparation of this document. Mr. Robert Schaffer, Director, Effluent Guidelines Division, and Mr. Gary E. Stigall, Branch Chief, Effluent Guidelines Division, Inorganic Chemicals Branch, offered guidance and suggestions during this project.

Appreciation is extended to the National Association of Photographic Manufacturers, Inc. and the individual companies and plants that participated in and contributed data for the formulation of this document.

250

SECTION X

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251

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253

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254

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~~X-10~~
260

SECTION XI

GLOSSARY

aeration: The addition of air to a liquid. This is done by pumping the liquid into the air or by bubbling air through it via sparging tubes. Aeration is used as part of the ferric EDTA bleach regeneration process in photographic processing. It can be used for reduction of oxygen demand in wastewater.

acid rinse: A solution, usually dilute acetic acid, used as a stop bath following development.

anion: The ion in an electrolyte which carries the negative charge and migrates toward the anode under the influence of a potential difference.

automatic wash water controls: Automatic solenoid operated shutoff devices which completely stop the flow of water into the processor when it is not being used, thereby avoiding excessive wash water flows.

biochemical oxygen demand (BOD₅): A measurement of the amount of dissolved oxygen an effluent will consume from water over a five-day period of time.

biodegradable: A substance capable of being broken down by organisms into simpler entities.

black and white film: This film consists of a support, usually a plastic film which is coated with a light sensitive emulsion and an outer protective layer. The emulsion is adhered to the supporting base with a special layer called a sub. The emulsion contains: gelatin, silver salts of bromide, iodide, chloride, sensitizers, hardeners, and emulsion plasticizers.

bleach-fix or blix: A solution used in some color processing that functions both as a bleach and as a fix.

bleach: A step in color film processing whereby the silver image is converted back to silver halides.

cation: The ion in an electrolyte which carries the positive charge and which migrates toward the cathode under the influence of a potential difference.

chelating agents: A class of chemical compounds that can form complex chemical species. Some of the compounds are used as bleaching agents when complexed with ferric ions and as sequestering agents in the isolation and removal of metallic ions.

chemical oxygen demand (COD): An analytical method for measuring the oxygen demand of an effluent. This method is faster than the BOD₅ test and responsive to a broader range of components.

chemical prewash: A salt bath between the fix and final wash which chemically removes the fix from the emulsion at a faster rate than can be done by washing, thereby reducing the after-fix wash water time and volume.

chlorination: The addition of chlorine to wastewater to cause breakdown of certain compounds by oxidation.

chromium: A metallic element whose compounds are used in some photographic processes as bleaching or hardening agents.

clarification: The process of removing turbidity and suspended solids by settling.

clearing bath: A processing solution that removes most residual fixer from processed film or paper prior to washing, minimizing the water requirement.

color couplers: A group of organic chemicals which react with the oxidized components of the developers to form color dyes. They are either incorporated in the film emulsion at the time of manufacture or they are included in the color developing solution.

color film: Color film has three separate light sensitive emulsion layers, which after inclusion of the appropriate sensitizing dyes, record an image of the blue light components on one layer, the green light

XI-2
262

components on another, and the red light components on the third layer.

color reversal (DC) process: A color reversal film process in which the color couplers are added during development.

color reversal (IC) process: A color reversal film and paper process in which the color couplers which form the color dye image are incorporated into the emulsion layers at the time of manufacture.

complex cyanide: This term refers to a complex ion containing cyanide ions and a cation such as iron, e.g., ferrocyanide $[\text{Fe}(\text{CN})_6]^{-4}$ and/or ferricyanide $[\text{Fe}(\text{CN})_6]^{-3}$.

conservation: Methods applied to make maximum use of processing chemicals and water and to keep the quantity of effluent discharged to a minimum.

continuous length processor: An automatic processing machine whereby long rolls of film or paper are fed into successive photoprocessing tanks via a series of appropriate crossover connections between racks. The starting end of the material to be processed is attached to a leader which guides the material through the machine.

conventional silver recovery: The use of metallic replacement or electrolytic methods or both for the recovery of silver from fix solutions.

countercurrent washing: A method of washing film or paper using a segmented tank system in which water is cascaded progressively from one tank segment to the next counter to the movement of the film or paper.

develop: A step in photoprocessing whereby the latent image is made visible in a developer solution.

developer: A chemical processing solution containing a developing agent. This solution converts the exposed portions of the photographic emulsion to silver, creating images of metallic silver.

developing agents: These photographic materials usually are aromatic compounds with phenolic or amino electron-donor groups arranged ortho or para with respect to each other, such as: hydroquinone, methyl p-amino-phenol (metol), or 1-phenol-3 pyrazolidone (phenidone).

dichromate bleach: A bleach used in some black and white reversal and color film processing.

dip and dunk: An automatic processing machine whereby strips of film are "dipped" into successive photoprocessing tanks and held for the appropriate time.

direct discharge: The discharge of wastewater to waters of the United States.

dissolved solids: Solid matter in effluent that will not settle out or separate with filtration.

drag-in: Water or solution carried into another solution by the film or paper being processed.

drag-out: Water or solution carried out of the processing tank by the film or paper being processed.

dry: The final processing step which involves drying the photographic film or paper in a dust-free atmosphere.

dye image: A color image formed when the oxidized developer combines with the color couplers.

EDTA (ethylenediaminetetraacetic acid): A chelating compound used in some bleach and bleach-fix solutions. It is also used in other solutions to sequester some ions present in hard water.

effluent: Liquid waste leaving its source.

electrolytic silver recovery: The removal of silver from silver-bearing solutions by application of a direct current to electrodes in the solution causing metallic silver to deposit on the cathode.

elution: (1) The process of washing out, or removing with the use of a solvent. (2) In an ion exchange process it

~~XI-4~~
264

- is defined as the stripping of adsorbed ions from an ion exchange resin by passing through the resin solutions containing other ions in relatively high concentrations.
- equalization: The collection of wastewater in tanks or ponds for the purpose of equalizing or controlling the flow quantities prior to discharge or other treatment steps.
- evaporation: A technique used to concentrate solids by removing water resulting in a quantity of concentrated waste containing the solids.
- ferricyanide: This ion, usually in the form of potassium ferricyanide, is used as a bleach for oxidizing metallic silver to ionic silver in some color processes. Ferricyanide is reduced to ferrocyanide as it oxidizes silver in the film emulsions.
- ferricyanide bleach: A processing solution containing the ferricyanide ion. This is used to convert metallic silver to ionic silver, which is removed in the fixing step.
- ferrocyanide: The ion that results when ferricyanide oxidizes silver or reacts with various reducing agents.
- filtration: The passing of wastewater through solid or particulate media to reduce the suspended solids.
- fix: A step in photoprocessing whereby the silver halides are removed from the emulsion using a solvent such as sodium thiosulfate.
- flocculation: The addition of a chemical, such as alum, ferric chloride or polymeric electrolytes, that promotes coagulation of suspended particles, thereby increasing settling rates and improving separation.
- gas-burst agitation: This is the most common method of automatic agitation found in automatic processing machines. Gas is released at controlled intervals through tiny holes in a distributor plate in the bottom of the solution tank. The gas bubbles formed during release provide the random agitation pattern necessary for uniform results.

~~XI-5~~
265

harden: This photoprocessing step serves to check emulsion swelling and raise the melting point for the emulsion to allow for drying at a higher temperature.

hardener: A chemical present in some photographic solutions that reacts with gelatin in the emulsion to protect the film from damage during or after processing. Common hardeners are potassium aluminum sulfate, potassium chromium sulfate, and formaldehyde solution.

ion: An atom or group of atoms possessing an electrical charge.

ion exchange: A reversible interchange of ions between a liquid and a solid involving no radical change in the structure of the solid. The solid can be a natural zeolite or a synthetic resin, also called poly-electrolyte. Cation exchange resins exchange their hydrogen ions for metal cations in the liquid. Anion exchange resins exchange their hydroxyl ions for anions such as nitrates in the liquid. When the ion-retaining capacity of the resin is exhausted, it must be regenerated. Cation resins are regenerated with acids and anion resins with bases.

low flow prewash: A system which concentrates most of the fix carryout in a low volume after-fix prewash tank. The system consists of segmenting the after-fix prewash tank to provide a small prewash section with separate wash water make-up and overflow.

metallic replacement: This occurs when a metal such as iron comes in contact with a solution containing dissolved ions of a less active metal such as silver. The dissolved silver ions react with solid metal (iron). The more active metal (iron) goes into solution as an ion and ions of the less active metal become solid metal (silver).

NAPM: National Association of Photographic Manufacturers, Inc.

National Pollutant Discharge Elimination System (NPDES): The Federal mechanism for regulating point source discharges by means of permits.

navigable waters: See waters of the United States.

negative process: A process which yields a negative image on film or paper of the original subject.

neutralization: The adjustment of the pH of a waste stream with acid or alkali to produce a near neutral condition.

non-process water: Water used for the heating and cooling of process solutions to maintain proper operating conditions or for the make-up water in cooling towers, boilers and lawn sprinkling systems. This water is not process water as it does not come in contact with raw materials or the product.

POTW: Publicly owned treatment works (45 FR 33423).

NPDES: See National Pollutant Discharge Elimination System.

on-site treatment: Treatment of effluent performed at its source, prior to discharge into a sewage system or a receiving body of water.

oxidation: The conversion of chemical substances to higher oxidation states through loss of electrons. In waste treatment, oxidation usually is involved in the breakdown of many substances.

ozonation: The process of using ozone (O_3) as an oxidizing agent to oxidize and degrade chemical constituents in an effluent or to regenerate ferricyanide bleach.

ozone: A powerful gaseous oxidizing agent (O_3); it can be generated by a high voltage discharge across a stream of air or oxygen.

persulfate: A strong oxidizing agent used to regenerate ferrocyanide to ferricyanide in bleaches.

pH: A numerical value describing the acidity (low pH number) and alkalinity (high pH number) of a solution.

polyelectrolytes: Synthetic chemicals (polymers) used to speed the removal of solids from wastewater by causing suspended particles to coagulate. They can be anionic

[- charge, nonionic (+ and - charge) or cationic (+ charge)].

precipitation: The separation of a dissolved substance from its solution by rendering it insoluble through chemical reaction.

prehardener: A solution used to harden the emulsion in order to protect it from damage during processing.

primary treatment: The removal of material that floats or will settle in municipal sewage by using screens to catch the floating objects and tanks for the heavy matter to settle in. This treatment usually involves sedimentation and/or flocculation.

process water: Water used in washing film and paper, in making up photoprocessing solutions, in the washing and rinsing of mixing utensils, storage tanks, and processing machines, and in area washdown.

reclamation: The process of deriving usable materials from waste, by-products, etc., through physical or chemical treatment.

regeneration: The removal or reconstitution of by-products and the replacement of certain components of the processing solution being reclaimed.

Rem-Jet: A coating on the back of certain films for the reduction of light reflections during exposure. The rem-jet backing is removed during processing by washing or by washing and mechanical buffing.

reversal process: A process which yields a direct positive image of the subject on the same material used for the original exposure.

reverse osmosis: A separation technique used for recovering wash water that involves letting a wastewater stream flow under pressure through a semipermeable membrane. Most of the water molecules pass through the membrane as permeate and the pollutants remain behind as concentrate.

XI-8
268

settling: The concentration of particulate matter in wastewater by allowing suspended solids to sink to the bottom.

short stop: A step in photoprocessing which follows development whereby the basic activators in the developer are neutralized to prevent further development.

silver halide: Silver halide is an inorganic salt of silver in combination with elements from Group 7A of the Periodic Table. Silver halide salts used in photography are silver chloride, silver bromide, and silver iodide. Upon exposure to light, silver halide crystals undergo an internal change making them capable of subsequent reduction to metallic silver by appropriate developing agents.

silver recovery: Removal of silver from used photographic processing solutions and materials so it can be made available for reuse.

spray washing: A method of washing film or paper using a spray rather than an immersion tank as a means of conserving water.

stabilizer: A chemical bath, usually the last in a processing cycle, that imparts greater life to a processed photographic film or paper through one of several preserving steps.

squeegee: A piece of flexible material or a thin stream of air set to impinge on one or both sides of photographic film or paper as it comes out of a tank of processing solution. This reduces the amount of solution carried over.

surface water: See waters of the United States.

suspended solids: Undissolved matter carried in effluent that may settle out in a clarifier.

total organic carbon (TOC): A measure of the amount of carbon in a sample originating from organic matter. The

test is run by burning the sample and measuring the carbon dioxide produced.

wash: A water wash is a step in photoprocessing removing residual processing chemicals absorbed in the emulsion or substrate.

waters of the United States: All waters which are currently used, used in the past, or may be used, for interstate or foreign commerce, including all waters subject to ebb and flow of the tide. Also includes intrastate lakes, rivers, streams, mud flats, and wetlands (44 FR 33300, 44 FR 33424).

zero discharge: A goal for 1985 as set by the Federal Water Pollution Act of 1972. This means that the discharge of pollutants into the navigable waters will be eliminated by 1985.

~~XI-10~~
270

APPENDIX A
TELEPHONE CONTACT SURVEY MEMO

~~A-1~~
271

(c) Other (such as coupler, developer, etc. _____
Processes used _____

5. Use of squeegees: Everywhere recommended _____ Partial use _____ Not used _____

6. Estimated Process Water Usage: less than 1,000 gpd _____; 1,000 to 9,999 gpd _____
10,000 to 99,999 gpd _____; more than 100,000 gpd _____.

7. Estimated production: less than 1,000 sq. ft./day _____; 1,000 to 2,999 sq. ft./
day _____; 3,000 sq. ft./day to 20,000 sq. ft./day _____;
more than 20,000 sq. ft./day _____.

B. Wastewater

1. Other than recovery or recycle, is process wastewater treated before
discharge? Yes _____ No _____

(a) If yes, how? _____

(b) Does the treated stream contain all the process wastewater? Yes _____ No _____

(c) Does the treated stream contain any non-process wastewater?

Sanitary _____ Non-contact cooling _____ Boiler _____ Other _____

2. Where are the wastewater streams discharged?

	<u>Contains</u>	<u>Discharged to</u>
Stream 001	_____	_____
Stream 002	_____	_____
Stream 003	_____	_____

3. Do you have a discharge permit for any stream?

Stream(s) _____

	<u>Number</u>
_____ state	_____
_____ Corp. Eng. Appl.	_____
_____ NPDES	_____
_____ Other (POTW)	_____

What parameters are limited? _____

A-3
273

4. Is analytical data available and for what period of time?
No _____ Yes _____ Period _____

5. Are sewer user charges employed by local municipality? If so, what are charges and basis (flow, pollutant, etc.) _____

C. General

1. Comments: _____

2. Would the plant be agreeable to an engineering visit by an EPA Representative?
Who should be contacted _____

3. What type of customer or service provided?
(a) Amateur _____
(b) Professional _____
(c) Commercial (Art, printing, etc.) _____
(d) Commercial (Movie, T.V.) _____
(e) Studio (portrait, school) _____
(f) Other _____

4. Are toners used? _____
If so what type _____

APPENDIX B
LONG-TERM PLANT EFFLUENT DATA

~~B-1~~
275

LONG-TERM DATA FOR PLANT 6208

KEY: AG79: Effluent Silver Concentration, mg/liter,
mid-1974 to July 1979
CN79: Effluent Total Cyanide Concentration, mg/liter,
mid-1974 to July 1979
CR79: Effluent Total Chromium Concentration, mg/liter,
mid-1974 to July 1979

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AG79

0.39	0.32	0.68	0.93	0.15	0.27	0.59	0.34	0.31	0.5
1.4	1.4	0.52	0.21	0.17	0.05	0.57	0.86	1.2	1.2
0.22	0.25	0.7	0.88	0.9	1.22	0.32	0.032	0.139	0.2
0.01	0.317	0.23	0.16	0.19	0.13	0.32	0.17	0.54	0.22
0.38	0.43	0.48	1.2	0.08	0.53	0.33	0.2	0.92	0.14
0.14	0.94	0.5	0.2	0.16	0.16	0.17			

CN 79

0.005	0.005	0.005	0.008	0.005	0.005	0.029	0.005	0.006	0.005
0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
0.005	67.4*	0.06	0.005	0.005	0.01	0.005	1.8	0.01	0.28
0.14	0.01	0.26	0.14	0.21	0.01	0.032	0.104	1.75	0.04
0.08	1.12	0.01	0.57	0.01	0.01	0.04	0.01	0.01	0.08
0.01	0.01	0.01	0.01	0.01	0.01	0.01			

CR 79

3.09	4.73	3.11	5.93	3.56	4.59	4.11	3.6	2.4	0.2
3.0	2.7	1.84	2.8	2.91	4.38	5.9	4.8	4.4	5.4
8.1	4.4	4.2	3.31	6.4	3.06	8.2	0.46	1.82	1.0
1.76	4.55	0.6	0.24	0.35	2.92	1.25	3.82	5.0	2.0
1.1	2.6	4.1	3.4	0.8	3.7	6.6	2.3	6.2	3.1
2.6	5.0	2.1	4.3	2.8	4.7	2.3			

* Value not used.

~~B-2~~
276

LONG-TERM DATA FOR PLANT 7781

KEY: AG577: Effluent Silver Concentration, mg/liter,
 1 February to 29 April 1977
 AG877: Effluent Silver Concentration, mg/liter,
 5 July to 1 August 1977
 CD577: Effluent Cadmium Concentration, mg/liter,
 1 February to 29 April 1977
 CD877: Effluent Cadmium Concentration, mg/liter,
 5 July to 1 August 1977

AG677									
6.31	5.10	5.27	9.75	4.64	8.64	13.12	7.93	7.26	7.94
7.50	8.10	4.44	3.28	2.33	4.46	2.36	3.15	4.33	3.70
5.76	8.46	7.46	3.03	4.34	2.72	1.40	1.97	2.46	6.20
5.60	8.00	2.85	6.10	9.27	15.10	14.68	5.78	4.23	2.91
11.66	10.34								
AG 877									
8.72	4.93	7.18	4.69	3.62	3.61	3.48	3.05	9.01	8.01
5.23	3.75	3.12	1.52	1.53	2.11	1.98	1.52	1.41	1.23
CD 577									
0.57	0.8	0.9	0.7	0.08	0.21	0.33	0.48	0.66	0.52
0.88	0.72	2.0	0.95	1.18	1.6	1.47	1.57	0.8	0.64
0.94	0.98	1.24	1.52	2.23	1.85	1.64	1.84	2.22	3.55
3.14	4.0	3.69	1.82	2.6	2.78	2.5	1.84	0.88	0.85
0.71	0.63	0.97	0.51	0.82	1.0	1.12	1.0	0.25	0.25
0.56	1.12	1.0	0.5	0.33	0.57	0.54	0.5	0.41	0.26
0.29	0.35	0.31	0.19						
CD 877									
0.18	0.19	0.24	0.18	0.1	0.09	0.09	0.11	0.17	0.22
0.2	0.15	0.12	0.04	0.04	0.04	0.05	0.06	0.02	0.05

B-3
277