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Preliminary Data Summary for the Photoprocessing Industry

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Acknowledgments

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1. Executive Summary

This Preliminary Data Summary for the Photoprocessing Point Source Category investigates the state of the industry and its wastewaters in relation to the existing 1976 Guidelines, and attempts to evaluate the relevance of these guidelines in the current photoprocessing operating and regulatory environment. The purpose of this document is to provide technical support towards a decision of possible revision of the 1976 Photoprocessing Effluent Limitations Guidelines and Standards. This study was conducted to meet the obligations of the Environmental Protection Agency (EPA) under section 304(m) of the Clean Water Act (CWA), in accordance with a consent decree in *Natural Resources Defense Council and Public Citizen, Inc.* v. *Browner* (D.D.C. 89-2980, January 31, 1992).

EPA promulgated an Interim Final Rule for the Photographic Category on July 14, 1976, establishing best practicable control technology currently available (BPT) limitations for one subcategory, the Photographic Processing Subcategory, at 40 CFR Part 459, Subpart A. Facilities falling within this photoprocessing subcategory use silver halide-sensitized photographic materials to produce continuous tone black-and-white or color negatives, positive transparencies, and prints for delivery to external customers. Commercial photoprocessing services are available through a variety of retail channels, including drugstores, discount/mass merchandisers, camera stores, mail order, and stand-alone mini labs. Photoprocessing also plays a major role in the businesses of portrait studios and motion picture production. About 100,000 establishment were identified in 1996 in Dun & Bradstreet under the commercial photoprocessing standard industrial classification (SIC) codes. Significant photoprocessing also occur as an ancillary activity within the health care profession at hospitals, dentists', doctors', and veterinary offices, and at noncommercial facilities such as schools, police departments, and to serve heavy construction and transportation needs. Combining all types of facilities, it is estimated that photoprocessing operations occur at 350,000 to 500,000 locations in the United States.

Data concerning the amount of film processed was available only for the commercial sector, which is estimated to represent 44 percent of total photoprocessing volume. For the commercial sector, it is reported that in 1994, 715.5 million rolls of film were processed, resulting in 17.58 billion exposures and generating revenue of over $5.5 billion. Over 92 percent of the film processed was 35mm format, and almost 95 percent was processed as color prints. Based on the commercial data, it is estimated that in 1994, 296 million square feet of film, and 4,120 million square feet of paper, were processed in the United States. The estimated water use by the commercial sector of this industry in 1994 is 2,250 million gallons. The major wastewater constituents of concern, with 1994 estimated commercial sector loadings, include sulfates (2.8 million lbs.), ammonia (3 million lbs.), silver (190 thousand lbs.), thiosulfate, and cyanide. Several technologies are available and employed to either treat the wastestreams, or as common in this industry, recover the chemicals and metals in the wastewater for resale or reuse. Recovery of silver is almost always practiced to some extent, both due to the value of silver and to comply with discharge regulations. Several silver recovery technologies are available, and the technology of choice depends on installation size and recovery requirements. The two most common methods are metallic replacement with the use of chemical recovery cartridges, and electrolytic recovery.

None of the hundreds of thousands of photoprocessing establishments have discharge permits that refer to the existing guidelines found at 40 CFR Part 459 Subpart A. The reason facilities are not covered directly by the guidelines is that only BPT regulations have been published, which cover direct dischargers. However, all except for a few large photoprocessors discharge to publicly owned treatment works (POTW), which requires pretreatment standards for existing sources (PSES) or pretreatment standards for new sources (PSNS) for coverage by the pretreatment standards. For the small percent of facilities that are direct dischargers, there is a production requirement that the facility process 1600 square feet per day or more of photosensitive film and paper. As a result of these factors the current guidelines are not applicable to virtually any photoprocessing facilities.

With the lack of any applicable national pretreatment standards for photoprocessing wastestreams, "local limits" as developed by the receiving POTW are the normal means of controlling photoprocessing discharges. The local limits are normally numeric and concentration-based, and frequently the only pollutant monitored in the indirect discharge permit is silver. The predominance of local limits to control photoprocessing discharges leads to a) mainly concentration based limits, b) variability from municipality to municipality on allowable discharge concentration, and c) possible changes in discharge limits based on changing water quality criteria or water body loadings goals. EPA has always encouraged the use of production-based rather than concentration-based limits for the control of photoprocessing wastewaters to promote water conservation.

There are questions concerning the environmental fate and effects of silver from photoprocessing wastes. Many of the stringent local limits are based on the highly dissociated and toxic silver nitrate. While silver nitrate is used in the production of photographic film and paper, it is not a characteristic pollutant of photoprocessing wastewaters. Rather, silver in photoprocessing wastewaters is characteristically in the form of silver thiosulfate complex, which has been shown to be about 20,000 to 40,000 times less toxic, on a concentration basis, to acutely exposed fathead minnows. The local limits may be overly stringent with regard to concentration of silver discharged, while lax on total mass of silver or other pollutants, due to lack of technical expertise and resources available at the local level. Further study is required to accurately predict the fate and toxicity of silver from photoprocessing wastestreams after entering a POTW.

2. Introduction

The purpose of this Preliminary Data Summary for the Photoprocessing Industry is to provide information for determining whether the existing technology-based effluent guidelines at 40 CFR Part 459 should be revised. This study describes the size and demographics of the industry, photoprocessing operations and the typical wastewaters generated, as well as the technologies available to treat these wastewaters. Total national pollutant loadings are estimated, and resulting environmental effects are qualitatively postulated. This information is presented against the backdrop of the existing technology-based guidelines and the utility of these guidelines to the permit writer.

Policy discussions and rankings with other industries for selection of guidelines revision are not subjects of this study. However, the material herein is a source of information for such future discussions and rankings.

This study was conducted to meet EPA's obligations under section 304(m) of the Clean Water Act, as implemented through a consent decree in *Natural Resources Defense Council et al.* v. *Browner* (D.D.C. 89-2980, January 31, 1992)(the "Consent Decree"). Pursuant to the decree, the Agency's latest biennial plan for developing new and revised effluent guidelines was published on October 7, 1996 (61 FR 52582), in which schedules were established for reviewing existing effluent guidelines and developing new and/or revised effluent guidelines for several industry categories. One of the industries selected for review of existing effluent guidelines was the Photographic Processing Point Source Category (40 CFR 459).

Specifics of the existing guidelines are presented in Chapter 3. This discussion explains that the existing guidelines are not relevant to the photoprocessing industry, due to the lack of pretreatment standards in an industry where most facilities discharge indirectly to a publicly owned treatment works. Chapter 3 then presents how, in lieu of applicable guidelines, local limits may be applied. Issues affecting the environmental performance of photoprocessors are also outlined.

A profile of the industry is given in Chapter 4, detailing what is considered a "photoprocessor," where these photoprocessors exist, and their relative market share. For certain segments of the industry, facilities are primarily engaged in photoprocessing, and these segments are identified by their Standard Industrial Classification (SIC) codes. Photoprocessing also occurs as an ancillary activity in a myriad of other public and private institutions as well. These institutions are identified, and data on market size and photoprocessing volume is presented.

Chapter 5 describes the basic photoprocessing operations. This leads into the discussion of wastewater sources and pollutant characterization in Chapter 6. Here, information and data are presented in an attempt to define the characteristic pollutants of photoprocessing wastestreams, and the volume of these wastestreams. Since no data has been gathered recently by the EPA to support the values presented, the characteristic pollutant list may not be accurate, and pollutant loadings based on flow rate and concentration can only be estimated. Further study, possibly including sampling of photoprocessing wastewaters, would be necessary to obtain more precise loadings values.

Chapter 7 presents the control and treatment technologies available to photoprocessors. Silver recovery and management systems are explained, as well as other practicable recovery methods such as color developer reuse and ferricyanide recovery. The economic motive as well as regulatory compliance motive for installing and maintaining such treatment and recovery systems is discussed.

Chapter 8 attempts to provide a qualitative assessment of the effect of discharging photoprocessing effluent on the environment. This is done by identifying the pollutants in the wastewaters, estimating their discharge quantities, and assigning toxic-weighted factors to these pollutants to arrive at toxic-weighted pound-equivalents. This analysis is followed with a caveat concerning the dependence of the toxicity of silver to the speciation of the silver, which dictates the oxidation state, solubility in water, and ionic dissociation in water, of the silver atom or molecule.

Again, the goal of this Preliminary Data Summary is to collate and put into perspective the readily available information and data concerning the photoprocessing industry. This study achieves its purpose in supplying information relevant to the existing guidelines in the current photoprocessing operating and regulatory environment, to aid in the decision of whether or not to revise the photoprocessing effluent guidelines.

3. Regulation of Photoprocessing Wastewaters

3.1 Existing Effluent Guidelines

EPA promulgated an Interim Final Rule for the Photographic Category on July 14, 1976 (41 FR 29078). The rule established best practicable control technology currently available (BPT) limitations for one subcategory, the Photographic Processing Subcategory at 40 CFR Part 459, Subpart A. The Agency determined that further subcategorization of photographic processors was unnecessary due to the similarity of pollutants discharged across the industry and that the pollutant loadings per unit of production among the studied facilities were in a relatively narrow range.

Subpart A covers "point source discharges resulting from the development or printing of paper, prints, slides negatives, enlargements, movie film, and other sensitized materials except that facilities processing 150 sq. meters (1600 sq. feet) per day or less are not covered." The scope includes both commercial and military facilities. Thus these regulations apply to facilities that directly discharge pollutants, but facilities that indirectly discharge to sewer systems are not covered.

EPA identified the major sources of wastewater from the industry as photo-processing solution overflows and wash waters. The rule listed the known significant pollutants as pH, total suspended solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD), cyanide and silver in various forms.

The technology basis for the limitations consisted of electrolytic silver recovery and bleach regeneration. In-plant measures to reduce silver and cyanide were included in the technology basis. EPA also considered basing limitations on biological treatment, but did not do so because of estimated cost impacts.

The BPT limitations at §459.12 are as follows:

Parameter	Daily Maximum	30-day average
	(kg per 1,000 m^2 of product)	
silver	0.14	0.07
cyanide	0.18	0.09
pH	Within range of 6.0 to 9.0	---

While most BPT regulations also set limitations for the conventional parameters BOD and TSS, the rulemaking notice stated that by controlling silver and cyanide, BOD and TSS are effectively co-treated, as well as COD.

The limitations are production based, based on the surface area of film or paper processed. The EPA determined that concentration based limitations where not appropriate for this industry because such limitations encouraged high water use and discouraged water conservation.

In the July 14, 1976 notice, the Agency stated its intent to publish a proposed rule covering best available technology economically achievable (BAT), new source performance standards (NSPS), and pretreatment standards for new sources (PSNS) for the industry. Such regulations would affect facilities that indirectly discharge wastewaters. It also stated it may propose regulations for the exempted smaller facilities. However, these regulations were never promulgated.[1]

EPA considered issuing effluent guidelines for other subcategories of the photographic industry, but no regulations were issued. For four subcategories, the Agency found very small quantities of toxic pollutants in the raw waste load: Diazo Aqueous, Diazo Solvent, Photographic Chemicals, and Thermal Products. The Silver Halide subcategory also had small quantities of toxics in the raw waste loads, and most of the facilities were direct dischargers, with NPDES permits that required effective treatment.(EPA 1981b)

It has been approximated that there are 350,000 to 500,000 facilities throughout the United States which process photographic films and papers.(Dufficy, Silver CMP) However, no permits are issued under 40 CFR 459 Subpart A. This is due to the fact that almost all photoprocessing facilities are indirect dischargers (discharge to a POTW), but only BPT has been published which covers direct discharges. Or if they are direct dischargers, their daily production may fall under the limit of 1600 square feet. Therefore, the existing regulations are not of utility to the permit writers.

3.2 Local Limits

In lieu of national pretreatment standards for the Photographic Processing Subcategory, POTWs may use local limits and the general and specific prohibitions established under the General Pretreatment Regulations (40 CFR Part 403). EPA developed the General Pretreatment Regulations under the Clean Water Act (CWA) to prevent the discharge to POTWs of pollutants

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[1] The Development Document contains chapters on BAT, NSPS and PSNS limits, although the regulations were never issued.

which will interfere with, pass through[2], or which are otherwise incompatible with the POTW (CWA § 307 (b)(1)). POTWs must establish, develop and enforce specific limits to implement the general and specific EPA prohibitions. The specific limits developed by the POTWs are commonly referred to as "local limits" and are enforceable pretreatment standards under the Clean Water Act.(§ 403.5(d))

Because, by definition within the context of 40 CFR Part 403, pollutant Pass Through or Interference results in a violation of the POTW's NPDES permit, the terms of the POTW's NPDES permit generally serves as a guide in establishing appropriate local limits to prevent such Pass Through or Interference. Accordingly, the effluent limits, water quality and sludge protection conditions, toxicity requirements, and operation and maintenance (O&M) objectives found in a POTW's NPDES permit generally establish the framework within which the POTW must operate in order to prevent Pass Through and/or Interference.

In determining the pollutants to be regulated in categorical pretreatment standards, another type of pass through analysis is performed. This analysis is based on the pollutants determined to be present in the wastewater discharges from the industry and is not restricted to only those pollutants contained in the POTW's NPDES permits.

The General Pretreatment Regulations also recognize that local limits which are more stringent than those set forth in the federal regulations may be established by state or local law. In addition, POTWs may choose to impose local limits which regulate categorical industries more stringently than under an applicable categorical standard, in which case the local limits will supersede the categorical standards as the applicable pretreatment standards.

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[2] "Pass Through" is defined as "a discharge which exits the POTW into waters of the United States in quantities or concentrations which, alone or in conjunction with a discharge or discharges from other sources, is a cause of a violation of any requirement of the POTW's NPDES permit (including an increase in the magnitude or duration of a violation)." 40 CFR 403.3 (n). "Interference" is defined as "a discharge which, alone or in conjunction with a discharge or discharges from other sources, both:

(1) inhibits or disrupt the POTW, its treatment processes or operations, or its sludge processes, use or disposal; and

(2) therefore is a cause of a violation of any requirement of the POTW's NPDES permit (including and increase in the magnitude or duration of a violation) or of the prevention of sludge use or disposal in compliance with the following statutory provisions and regulations or permits issued thereunder (or more stringent state or local regulations): Section 405 of the Clean Water Act, the Solid Waste Disposal Act (SWDA) (including Title II, more commonly referred to as the Resource Conservation and Recovery Act (RCRA), and including state regulations contained in any state sludge management plan prepared pursuant to Subtitle D of the SWDA), the Clean Air Act, the Toxic Substances Control Act, and the Marine Protection, Research and Sanctuaries Act." 40 CFR 403.3 (i).

While local limit development is required of POTW's under the Clean Water Act and the General Pretreatment Regulations, neither the federal statute nor the regulations mandate the type of local limits to be established. Instead, as EPA has recognized in its rulemakings under the General Pretreatment Regulations, the establishment of local limits is a matter primarily of local concern which should be left to the discretion of the POTW.(see 46 FR 9494, 9415, Jan. 28, 1981, and 52 FR 1586, 1593, Jan. 14, 1987) To help with local limit development, EPA has issued the "Guidance Manual on the Development and Implementation of Local Discharge Limitations Under the Pretreatment Program."(EPA 1987) Through this guidance, EPA has indicated that POTWs are to use site-specific data to identify pollutants of concern which might reasonably be expected to be discharged in quantities sufficient to cause POTW or environmental problems. Once the pollutants of concern and the sources discharging these pollutants have been identified, the POTW must select the most effective technical approach for the development of its local limits.

While numeric limits have traditionally been used for local (non-categorical) limits, they are not required by federal statute or regulation. One alternative approach for local limit development identified by EPA in its guidance is the use of industrial user management practice plans. Through this approach, a POTW can require dischargers to develop and implement management practice plans covering their handling of chemicals and wastes. Once incorporated into local laws and regulations, these plans become an enforceable pretreatment requirement.

The majority of the photoprocessing facilities are small in size (having fewer than ten employees), and typically discharge less than 1,000 gallons of wastewater per day. For the most part, these photoprocessing indirect dischargers do not meet the definition of a "Significant Industrial User" (SIU) in the General Pretreatment Regulations because no pretreatment standards have been incorporated into 40 CFR Part 459 and their discharge of process wastewater is less than 25,000 gallons per day and/or 5% of the hydraulic or organic capacity of the POTW.(§ 403.3 (t)) While individual photoprocessors can be designated an SIU by a POTW, the burden of demonstrating that an individual photoprocessor "has a reasonable potential for adversely affecting the POTW's operation or for violating any pretreatment standard or requirement" is high.

3.2.1 Local Limits on Silver

Silver was identified as a "priority pollutant" in the Clean Water Act of 1977 (CWA 307 (a)(1)), following an earlier listing of silver as a drinking water contaminant by the United States Public Health Service. EPA issued water quality criteria for silver in 1980.(EPA 1980) In 1987, amendments to the CWA required EPA and the states to establish water quality standards and to set, where necessary, water quality based effluent limitations for priority pollutants, including silver, which were causing water quality problems (CWA 304(l)). As a result, POTWs are beginning to receive monitoring requirements and/or numerical limitations for silver in their NPDES permits. At the same time, POTWs are finding, through their headworks loading analyses, discharger surveys and other analyses, that much of the silver is being discharged by numerous small sources such as domestic, institutional and commercial sources which are more difficult to control than photoprocessors. When taken as a whole, photoprocessors have been found to be a major source of silver. In most cases, silver is the only pollutant in photoprocessing wastewaters which is subject to local limits.

Since virtually all photoprocessors are not covered by national categorical standards, local limits are the normal route to control the pollutants discharged by photoprocessors. In an attempt to provide both photographic processors and POTWs with a cost-effective alternative to numeric limits and monitoring, the Silver Council, which is an industry association, and the Association of Metropolitan Sewerage Agencies (AMSA) have developed a "Code of Management Practice for Silver Dischargers" (Silver CMP). The Silver CMP provides recommendations on technology, equipment and management practices for controlling silver discharges to POTWs. The practices recommended vary with the size of the photoprocessor, defined by flow volume of silver-rich solution and wash water. Through the use of its alternative compliance mechanisms, the Silver CMP encourages use of pollution prevention technologies, such as water conservation methods.

The Silver CMP encourages the development of industry-wide performance standards for silver recovery systems that maximize silver recovery and minimize its release to the environment. The recommended practices are defined by a minimum recovery of silver from silver-rich processing solutions (e.g., 90 percent) and alternative combinations of recovery methods that would achieve those recovery rates. Those developing the Silver CMP estimate that compliance with the recommendations would reduce silver loadings to POTWs by 25 to 50 percent. Three municipalities have implemented the Silver CMP: Albuquerque, NM; Colorado Springs, CO; and New York , NY. Over a dozen other municipalities are planning to implement or have expressed an interest in implementing the recommendations of the Silver CMP. However, data have not been provided to EPA to demonstrate the reductions in silver and other pollutants discharged upon implementation of the Silver CMP. Currently (1996), the Silver Council and AMSA propose to jointly conduct, with EPA, a 3-year program to implement and measure the effectiveness of the Silver CMP in 5 to 7 cities of various sizes throughout the United States.

The existence and acceptance of the Silver CMP, and the results of the Silver CMP demonstration project, will not necessarily have an effect on any future effluent guidelines development for the photoprocessing industry. In part, this is due to the different means of the two pollutant discharge control ends: single pollutant versus multi-pollutant, and local evaluation and acceptance versus national rule.

3.3 Regulatory Drivers and Barriers

A study completed by the EPA in 1994 investigated the factors influencing the environmental performance of the photoprocessing industry. The goal of the study was to determine what factors act as incentives to improve environmental performance (drivers) and what factors act as barriers or disincentives to improving environmental performance. Some of the issues raised in the report are outlined below. For the details of the analysis the report should be reviewed.(EPA 1994)

The report notes that a number of factors contribute to the low local limits concentration for silver that are imposed in many locations. First, the federal water quality standard is based on the toxicity of ionic silver. The federal concentration limit for silver in aqueous effluent is 5 parts of silver per million parts of water. Again, this limit is based on tests performed with silver nitrate in laboratory test water, which yields ionic silver. However, silver nitrate is not a characteristic pollutant of photoprocessing wastewater. Rather, silver thiosulfate is the characteristic form of silver, and silver thiosulfate has been shown, on a concentration basis, to be thousands of times less acutely toxic to fathead minnows than silver nitrate.(Dufficy) Currently there are no reliable analytical procedures to test for ionic silver, so that for the time being monitoring and compliance are necessarily based on total recoverable silver. Also, pretreatment permit limits are practically always expressed on a concentration rather than mass basis, which discourages adopting water saving measures such as "washless" technologies or otherwise reducing water use.

The report also notes that the regulation of silver-bearing wastes under the Resource Conservation and Recovery Act (RCRA) increases transportation costs of some photoprocessing wastewaters to central treatment facilities for silver recovery, and increases the burden of storing wastewaters and shipment off-site for centralized waste treatment. On the other hand, photoprocessors can avoid RCRA regulation by treating and discharging their wastes in compliance with Clean Water Act requirements. These factors, reportedly, discourage the recycling of silver, discourage the efficient treatment of photoprocessing wastewaters in centralized treatment facilities, and encourage discharge of these wastewaters to POTWs. It is claimed that removal of silver from the RCRA Toxicity Characteristic list would eliminate most of the added burden, encouraging increased recycling of silver and centralized treatment of photoprocessing wastewaters.

4. Photoprocessing Industry Profile

4.1 Photoprocessing Industry Overview

The photoprocessing industry, for the purpose of this study, consists of photographic processors using silver halide-sensitized photographic materials to produce continuous-tone black-and-white or color negatives, positive transparencies, and prints for delivery to external customers. The main industrial segments to which this study applies are as follows. "Photofinishing Laboratories" (SIC 7384), consists of facilities primarily engaged in film developing and print processing for the trade or the general public. 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 primarily engaged in providing commercial photography services for advertising agencies, publishers, and other business are classified in "Commercial Photography" (SIC 7335), and those providing commercial art or graphic design services for advertising agencies, publishers, and other business are classified as "Commercial Art and Graphic Design" (SIC 7336). The processing of motion picture film falls under "Services Allied to Motion Picture Production" (SIC 7819).[3]

In the industries mentioned above, a significant portion of total revenue is in general derived through the processing of photographic films, slides, and prints. However, as in SIC 7336 and 7819, photoprocessing may occur along with other significant revenue-generating activities. Photoprocessing operations also occur in a myriad of other public and private institutions, such as dental offices, hospitals, police departments, industrial X-ray services, and schools. As an example, Table 4.1 shows the number of photoprocessing facilities by type for Phoenix, Arizona. In the health care and noncommercial sectors, the processing of photographic films and papers is an ancillary activity, whereas in the commercial sector it is the main activity.

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[3] The terms "photoprocessing," "photofinishing," and "photo developing" are interchangeable. For consistency, the term "photoprocessing" is used throughout this report.

Table 4.1 Number of Photoprocessing Facilities by Type for Phoenix, Arizona

Facility type	Number of facilities by size (in number of employees)			
	Small (1 to 19)	Medium (20 to 49)	Large (50 to 499)	(More than 500)
Health Care				
Hospitals[a]	14	1	61	32
Dentists	1,422	16	1	0
Doctors	915[b]	122	47	2
Veterinarians	278	9	2	0
Chiropractors	515	6	0	0
Commercial				
Minilabs	184	0	0	0
Photofinishers	0	5	5	0
Prof. Labs	129	9	2	0
Motion Picture	1	0	0	0
Microfilm	12	3	1	0
Graphic arts	783	101	47	3
Noncommercial				
Schools	0	0	5	7
Police Dept.	4	3	18	11
Heavy Construction.	269	57	58	4
Transportation	14	2	44	7
Fabricated Prods.	18	5	42	10
Finance/insurance/ real estate	0	0	22	10
Jewelry/silverware/plated ware	47	1	0	0

[a] Does not include university, college, or public hospitals.

[b] Include offices of podiatrists, osteopaths, and 10% of all medical doctor offices.

Source: WEF 1994

Combining all types of facilities, it is estimated that photoprocessing operations occur at 350,000 to 500,000 locations in the United States.(Dufficy, Silver CMP) The number of establishments identified under the commercial photoprocessing SIC codes mentioned above are listed in Table 4.2 below.

Table 4.2 Number of Photoprocessing Establishments by SIC Code, 1996

Standard Industrial Classification (SIC)	SIC Description	Number of Establishments	
		As Primary Business	As Primary or Secondary Business
7384	Photofinishing Laboratories	10,430	13,171
7221	Photographic Studios, Portrait	27,607	32,184
7335	Commercial Photography	14,845	18,414
7336	Commercial Art and Graphic Design	31,476	37,264
7819	Services Allied to Motion Picture Production	7,656	9,187
	Total:	92,014	110,220

Source: Dun & Bradstreet

Photographic films and paper are used mainly for the following reasons: a) to diagnose medical problems, b) to diagnose structural defects of buildings, bridges, and roads, c) document, record, and transfer information, and d) record personal events and preserve memories. The market for photographic services and supplies can be divided into three major segments:

- Medical applications
- Graphic arts, and
- Amateur photography, served by commercial sector

Medical users include large hospitals and diagnostic clinics, as well as doctors' and veterinarians' offices. The largest single user in the medical market is the Veterans Administration. The graphic arts industry consists mainly of printers who are partially involved in photoprocessing. These businesses serve an industrial market through published documents and advertising. In most cases, photography represents a small part of their business and does not present their most pressing environmental concern. The amateur photography sector includes all amateur photographic processing, whether at minilabs, large wholesale laboratories, or mail order processing labs. These labs serve individuals taking pictures mainly to preserve memories.

There are the variations among the demands of the three major market segments--medical imaging, graphic arts, and amateur photography. These requirements affect the constraints on process and product improvements:

- The medical market is concerned with rapid and accurate diagnosis, and therefore requires both quality and speed, as well as longevity of the image.
- The graphic arts market requires high quality pictures, but is relatively unconcerned with processing speed.
- The amateur market tends to be more concerned with speed in processing, but demands increasingly higher quality.

In lieu of revenue and photoprocessing volume data, the relative size of these segments can be inferred from information of silver consumption. Data on the allocation of silver for various photographic uses for 1993 are shown in Table 4.3 below.[4]

Table 4.3 Photographic Use of Silver, 1993

Photographic End-Use	Silver Demand: U.S., Japan, and Western Europe (Million Troy Ounces)	Percent of Total Photographic Silver Demand
Amateur Picture Taking (Commercial)	82	44%
Medical, Excluding Dental	46	25%
Graphic Arts	41	22%
Industrial and Dental	17	9%
Source: WSS 1993		

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[4] It has been reported that in 1995 the Photographic Industry consumed 29 percent of total worldwide silver fabrication, for the production of photographic film and paper.(WSS 1996)

4.2 Photoprocessing Volume and Revenue: Amateur Market

Information on amateur photoprocessing volume and revenue is presented below. These data exclude health and noncommercial photoprocessing because data were not available for these segments. As shown in Table 4.3, by correspondence to silver use it is estimated that the amateur market accounts for 44 percent of total photoprocessing volume.

In 1994, the total number of rolls processed was 715.5 million, resulting in 17.58 billion exposures. The predominant film format of choice was 35mm, making up 92.1 percent, and color prints were the most popular film type, capturing 94.7 percent, of exposures processed in 1994. Tables 4.4 and 4.5 show the market share of the various film formats and film types.(PMA 1995)

Original prints are normally 3 ½ by 5 inches or 4 by 6 inches, and they can be either single prints or twin prints. Having plateaued at 36 percent from 1991-93, 4" by 6" print market share jumped 4.5 points in 1994, accounting for 40.6 percent of prints. Twin prints, following a 2.4 point climb in 1992, and gaining 2.7 points in 1993, experience stable market share in 1994, with 46.6 percent. Over three-quarters of photofinishing sales dollars came from original prints, while reprints and enlargements accounted for 14 percent.(PMA 1995)

This amateur or commercial photoprocessing occurred through various retail channels, such as drugstores, stand-alone mini-labs, and mail-order processors. The breakdown of market share within each of the retail channels is shown in terms of roll share in Table 4.6, and in terms of dollar share in Table 4.7. Years 1993 and 1994 are provided to show the industry trends. As Table 4.7 shows, consumers spent $5.5 billion on photoprocessing in 1994. In 1993, stand-alone mini-labs had the highest revenue spot, but were overtaken by drugstores in 1994. The discount/mass merchandiser channel out paced gains made in all other channels, with its dollar share up 2.9 percentage points. Photoprocessors compete based on price, quality, convenience, and speed of processing. The trends in demand for amateur photographs are somewhat cyclic and follow the economic cycles, with a minimum customer base below which demand will not fall. When people become more price sensitive, as in a recession, they are more willing to sacrifice convenience and speed for lower prices. (EPA 1994) The characteristics of the various types of labs are summarized in Table 4.8.

Table 4.4 1994 Photoprocessing Total Exposures by Film Format

Film Format	Number of Exposures (Millions)	Percent of Exposures
35mm	16,190	92.1%
110/126	1,195	6.8%
Disc	123	0.7%
Other	70	0.45%
Total	17,580	100%

Source: PMA 1995

Table 4.5 1994 Photoprocessing Total Exposures by Film Type

Film Format	Number of Exposures (Millions)	Percent of Exposures
Color print	16,648	94.7%
Slide	615	3.5%
Black & White	316	1.8%
Total	17,580	100%

Source: PMA 1995

Table 4.6 1993 and 1994 Market Share of Photoprocessing by Retail Channel

---Roll Share---				
Retail Channel	**Number of Rolls(Millions)**		**Percent Share**	
	1993	**1994**	**1993**	**1994**
Drug Store	183.8	188.9	26.5%	26.4%
Stand-Alone Minilab	104.3	98.4	15.0%	13.8%
Camera Store	56.0	52.2	8.1%	7.3%
Discount/Mass Merchandiser	176.9	202.6	25.5%	28.3%
Supermarket	98.0	96.2	14.1%	13.4%
Mail Order	53.1	54.8	7.7%	7.7%
Other	22.0	22.5	3.2%	3.1%
Total	694.0	715.5	100.0%	100.0%

Source: PMA 1995

Table 4.7 1993 and 1994 Market Share of Photoprocessing by Retail Channel

---Dollar Share---				
Retail Channel	**Retail Dollars (Millions)**		**Percent Share**	
	1993	**1994**	**1993**	**1994**
Drug Store	$1,356	$1,359	24.8%	24.5%
Stand-Alone Mini-Lab	$1,398	$1,296	25.5%	23.4%
Camera Store	$734	$699	13.4%	12.6%
Discount/Mass Merchandiser	$871	$1,039	15.9%	18.8%
Supermarket	$649	$653	11.9%	11.8%
Mail Order	$289	$312	5.3%	5.6%
Other	$177	$180	3.2%	3.2%
Total	$5,475	$5,538	100.0%	100.0%

Source: PMA 1995

Table 4.8 Characteristics of Amateur Film Processing Labs

Lab Type	Price	Quality	Processing Speed
Minilabs	Two to Three Times Higher than Others	Lower than Others	One Hour
Wholesale Labs (Drug Stores, Grocery Stores)	Medium	Equal to Minilabs	Two to Three Days
Mail Order Labs	Low	High	One Week

Source: EPA 1994

Consolidation is occurring in the industry, both from a manufacturing perspective and from a processing perspective. Some smaller manufactures have been absorbed by the large market players. In addition, some manufactures are now involved in processing. Kodak owns approximately half of Qualex Incorporated, which is the largest single photo processing company. Fuji and Konica have also purchased photo processing labs. As a result, the three largest manufactures are now also full or partial owners of the three largest photoprocessing chains.(EPA 1994)

Compared to large labs, smaller labs have a limited capital base, and hence tend to be somewhat less sophisticated. Industry representatives point out that the trend toward concentration among photoprocessing labs over the past several years is largely a result of restrictive environmental standards. They claim that compliance has become prohibitively expensive for small operations to achieve.

While stand-alone mini-labs are listed as a separate retail channel, mini-labs are also found in all other retail channels as well. Industry data distinguish between retail mini-labs, regardless of retail channel, versus the larger wholesale, captive, and mail order labs. The data show that the number of minilabs has grown rapidly over the past decade, from approximately 800 in 1981 to 18,900 in 1994. In 1994, minilabs were located in 3,100 camera stores, 6,124 stand-alone minilab outlets, and 5,153 mass-retail stores. This indicates a significant increase in the number of mini-labs in mass-retail stores. The number of mini-labs in other types of stores declined slightly over the same period. In 1994 these mini-labs processed 214.2 million rolls, accounting for 30 percent of the total 715.5 million rolls, while the wholesale, captive, and mail order labs processed the remaining 70 percent. The mini-labs also proved more profitable, receiving 43.8 percent, or $2,426 million, of the total $5,538 million in revenue and wholesale, captive, and mail orders made the remaining 56.2 percent or $3,112 million.(PMA 1995) Thus, while mini-labs processed just 30 percent of the rolls, they collected 43.8 percent of the total revenues.

4.3 Production of Photosensitive Papers and Films and Photoprocessing Equipment

The photographic equipment and supplies industry is not covered in this study. This category is mentioned here because of the interface with photoprocessors, and to explicitly describe what is and is not covered in this study.

Facilities classified under SIC 3861, "Photographic Equipment and Supplies," produces a wide variety of products for the photoprocessing industry, including photosensitive plates, film, paper, and cloth, photographic chemicals, and photoprocessing equipment. While the photoimaging industry is highly diffuse on the processor side, it is highly concentrated on the manufacturing side. A Dun & Bradstreet count in 1996 indicated 974 establishments under SIC 3861 as a primary business, and 1,254 establishments under SIC 3861 as a primary or secondary business. Manufacturers with significant operations in the United States include:

- Eastman Kodak Company
- Polaroid Corporation
- 3M Corporation

- Xerox
- Ilford (owned by International Paper)
- Anitec Image (also owned by International Paper).

Kodak is by far the largest U.S. manufacturer. Polaroid Corporation is the second largest but their primary film product is instant film.(EPA 1994)

As a whole these companies gain more revenue through the sale of photographic nondurable goods of film, paper, and photoprocessing supplies, than through the sale of processing equipment. The 1992 Census of Manufacturers data shows that the value of shipments of supplies of film and paper was $4,545 million, but that of the processing equipment was only $547 million.(EPA 1994)

Manufacturers and processors have a close relationship in this industry. Processors rely heavily on manufacturers for compliance assistance and innovations to address environmental and regulatory concerns. Manufacturing is driven in part by the demands placed upon the processors, both by regulators and by the end consumer. Manufacturers supply processing systems which include both equipment and supplies to customers. Photoprocessors do not have to purchase supplies from the same manufacturer that supplied the equipment, but many, especially the smaller minilabs, often do. All of the manufacturers have support systems to assist the processors with operations and environmental compliance. Such systems include instructional seminars, facility compliance evaluations, and compliance kits.(EPA 1994)

4.4 New Technologies in Photography: Advanced Photo System and Digital Imaging

Two new technologies are introduced here because they may affect the volume of photographic film and paper processed in the future: Advanced Photo System (APS) versus the relative growth of digital imaging (DI). APS represents an evolution of silver halide technology while DI, utilizing electronic means of image capture and storage, represents a threat.

The APS system was launched in April, 1996, on basis of a new film format with a number of features designed to improve and simplify photography. The most significant improvements will be the choice of three different print layouts, and the ability to select frames for printing from an initially produced sheet of miniature prints as opposed to awkward negatives. The new film cartridge is "dropped" in for simpler loading, and adds features such as a disk to store various types of film information. For example, this information can be used by the cameras to adjust for lighting conditions, and allows the film to be removed mid-real and reloaded later on without accidental double exposure. The reverse side of the film has a transparent magnetic layer which can record digital information to be used by the photoprocessing equipment. Although each frame of film will capture the full image entering through the lens, the selection of different print layouts allows the processor to magnify a suitable area of the frame to produce prints with a range of aspect rations. The film itself is made from a stronger and thinner base and is coated with more advanced emulsions.

In terms of photoprocessing volume the most important question is whether the APS will encourage more prints to be made because of ease of frame selection from the miniature preview prints and wide range of print layout options, or less prints due again to selection from the miniature previews.

Market penetration by digital photography is perceived as a threat to silver halide-based photography, but this emerging technology faces two significant quality problems. These are the inferior and expensive image capture and the low quality of the output medium. DI would lead to a decrease in film and paper photoprocessing volume because the film is replaced by a semiconductor chip known as a charge-coupled device. The photographs are then downloaded onto computer on which they can be manipulated and printed on thermal or ink-jet paper. The quality of the image is directly proportional to the number of photocell elements in the charge-coupled device, which ranges from 250,000 in amateur cameras to over 6 million in the professional market. By contrast, the average 35 mm negative contains approximately 10 billion silver-halide crystals. As of 1996 cameras introduced for the amateur market cost in the region of $1,000 and produce images of up to 756 by 504 dots or pixels, making them suitable for amateur use on a computer screen, but unacceptable for large prints. However, much more expensive digital cameras have become fairly popular with photojournalists, who can now send photographs across the world via mobile phone and computer links. The most significant impact of digital photography on silver-halide photoprocessing volume may come from the medical X-ray sector. Some hospitals are investing heavily in sophisticated computer equipment to replace the conventional X-ray light box.(WSS 1996)

The effects of DI on silver halide-based photoprocessing volume are beginning to be seen. While the production of X-ray film increased marginally in 1995 for both domestic and export markets, manufacturers reported that growth has been curtailed by digital imaging. In the graphics art sector, photographic paper consumption was down 2 to 3 percent, reportedly because of the impact of digital imaging. The future tends of DI market share are, of course, speculative. However, due to the simplicity and lower cost inherent in silver-halide technology, it appears that this traditional technology will not be overrun by DI in many of the major photoprocessing markets, such as amateur photography.(WSS 1996)

5. Description of Photoprocessing Operations

5.1 Process Descriptions

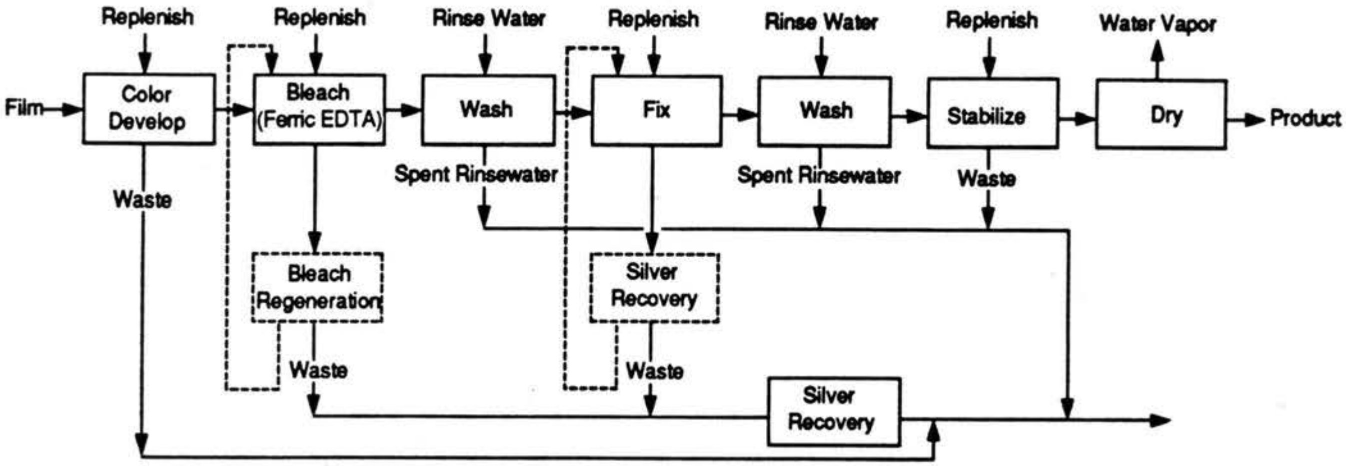
The processing of photographic film and paper requires the use of a number of chemicals to develop and produce finished photographic goods. The waste streams generated vary widely according to the type and volume of processing. Photoprocessing is dominated by color print film, prints, and slides, with only about 10 percent of the market involving black-and-white processing. Because color processing usually represents a greater production volume of the operations at a given location, it usually generates a larger waste stream volume. An increasing portion of the color market is being taken by mini-labs, which are automated machines that occupy little space. These machines are the ones used by the popular one-hour developing centers. The waste stream volume from most one-hour developing centers has been greatly reduced, because most centers have converted to "washless" or "plumbingless" processing, which does not use a conventional wash cycle.(EPA 1991a)

5.1.1 Color Processing

Film and paper used for color photography consist of three separate layers of photosensitive emulsion with intermediate layers. The emulsion layers are coated on clear film base or on paper, and each layer is sensitive to either red, green, or blue light due to the presence of selective dyes in the emulsion. Intermediate layers filter out other wavelengths, so that the silver halide salts in each photosensitive layer are exposed only to light of the specific color. A colorless dye-forming coupler is present along with the silver halide crystals in each emulsion layer. When processed in a color-developing solution, an image of "developed silver" is formed in each layer. The exposed silver halide crystals are reduced to metallic silver, while simultaneously producing oxidized developer molecules. The oxidized developer reacts with the dye-forming coupler to produce a dye which is complementary in color to the light to which the emulsion layer is sensitive. The intensity of the dye formed in a particular portion of the image is dependent on the quantity of oxidized developer, which is in turn proportional to the extent of exposure in that area.

A bleach bath renders the color image visible by converting the black metallic silver image back to a silver halide. All of the silver on the film, whether exposed or not, can then be dissolved and removed in the fixer bath. The dye is retained in each layer of the film so that a negative (complementary) color image remains. Some processes combine the bleach and fix processes in a single solution, termed bleach-fix or "blix." It is a common practice to introduce the film into a stabilizer bath after the fixer solution to equilibrate the emulsion and increase the stability of the dye image to light. A schematic diagram of the color negative film process is shown in Figure 5.1.(EPA 1991a)

Figure 5.1 Color Negative Film Process



Positive color prints can be made from the film negative recorded by the camera by exposing color paper or other suitable print medium to light passed through the developed film. The print medium, which contains the same combination of colorsensitive emulsion layers as does the film, is then processed through a similar sequence of solutions to obtain the final print, as illustrated by Figure 5.2.(EPA 1991a)

For color slides, a positive color image is produced directly on the film by reversal processing. The exposed color film is first subjected to black-and-white processing to produce a negative image consisting only of metallic silver. After washing, the film is immersed in a reversal bath that renders the remaining silver salts developable. The film is then processed in a color developer that reduces the remaining silver salts and produces a positive dye image. Then a sequence of bleach, fixer, and wash steps produces the final color transparency. Color prints can be made directly from positive slides by a similar reversal process. Figure 5.3 is a schematic diagram depicting both slide and reversal print operations.(EPA 1991a)

Cinemagraphic film processing is similar to processing of color print or slide film. In commercial operations, a large number of copies are made from one film. A print or "negative image" film is used for the original exposure and then used to make film copies (much as print film is used to make prints). Amateur film processing, which usually results in only one copy of the film, uses film much like slide film that is exposed and processed, producing the positive image on the originally-exposed film.

Figure 5.2 Color Negative Paper Process

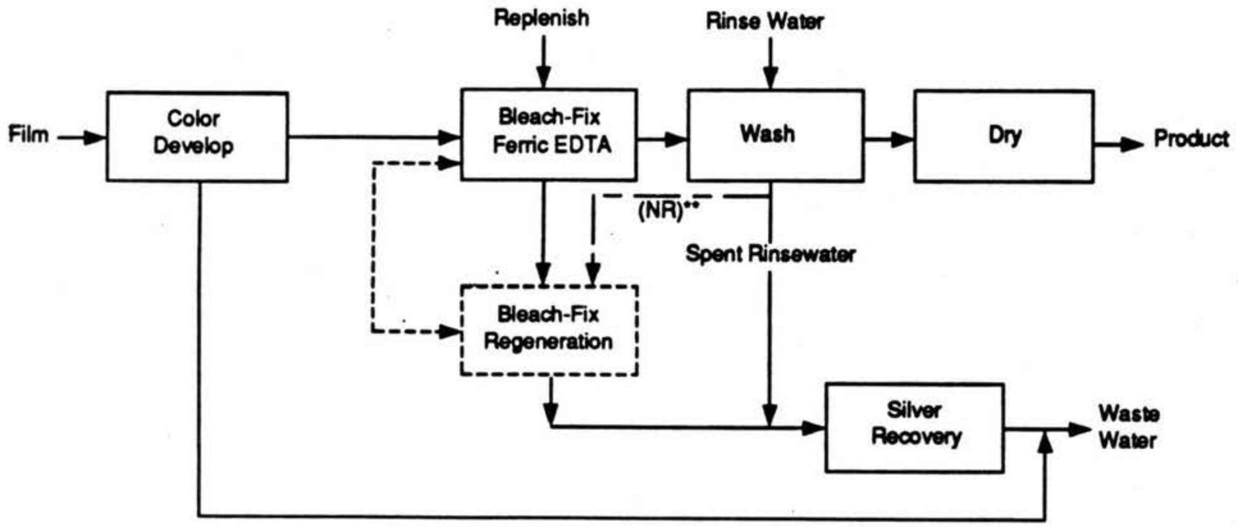
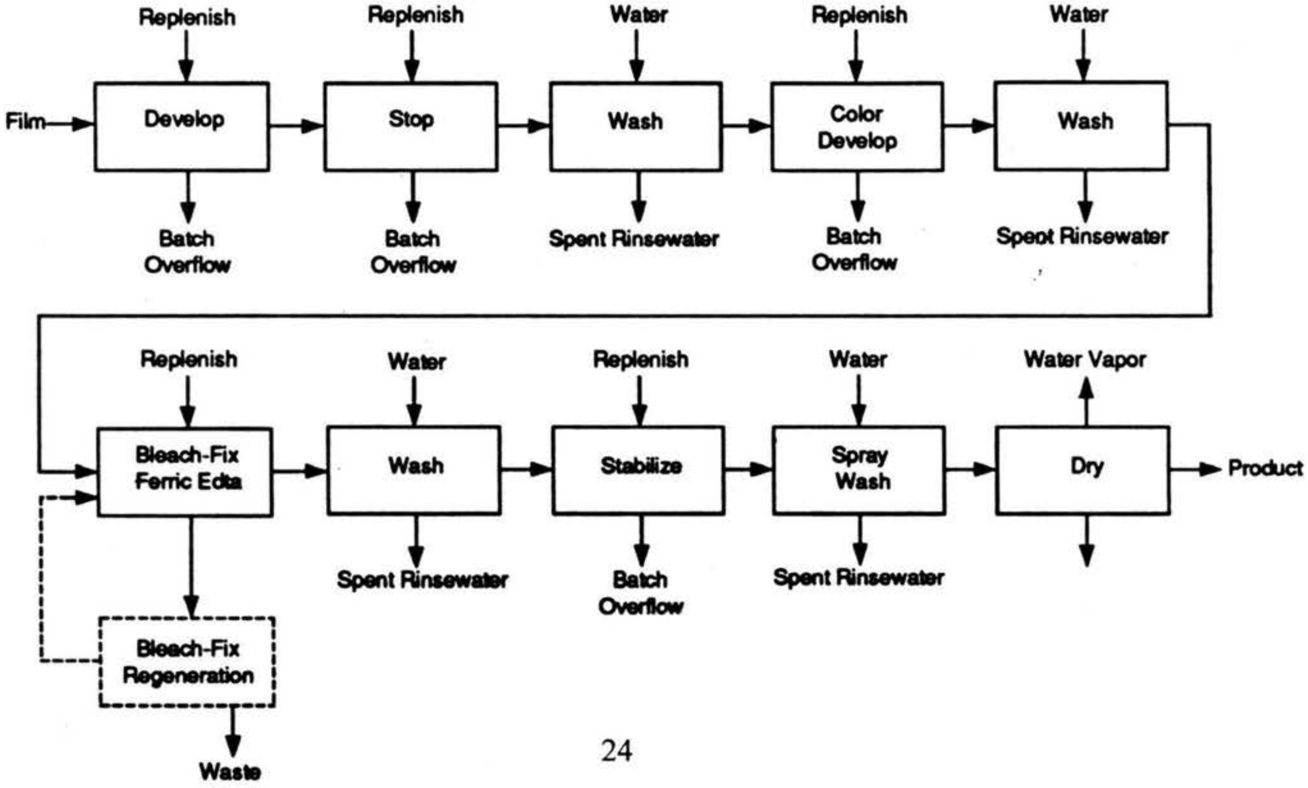


Figure 5.3 Color Reversal Paper Process



5.1.2 Black-and-White Processing

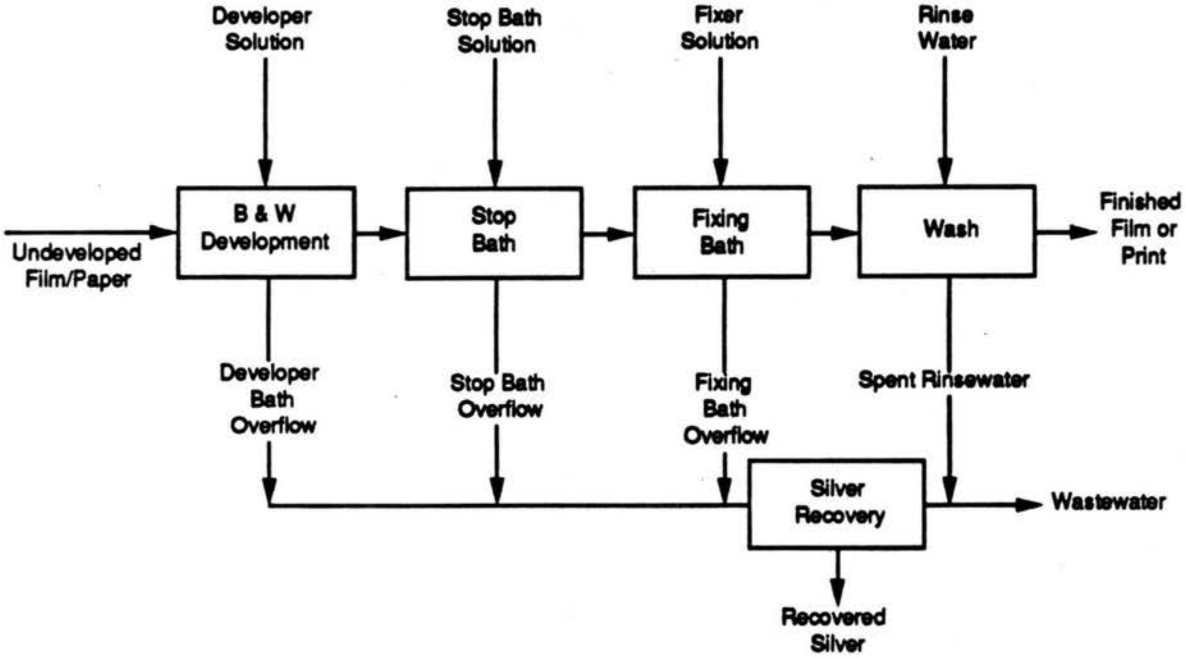
The photosensitive medium used for black-and-white processing is an emulsion composed of a dispersion of fine silver halide crystals in a matrix of gelatin. This emulsion is applied in a layer approximately 1/1000 of an inch thick on a supporting material, either paper or clear plastic film. Brief exposure to small quantities of light produces a chemical change in the silver halide crystals, which allows the silver ions in the exposed crystals to be converted to metallic silver at a faster rate than in unexposed crystals. By focusing the light through the camera lens, the pattern of exposed crystals corresponds to the image from which light is reflected. At this point, the exposed silver halide crystals are termed "developable." When the film is subsequently immersed in the developing solution, composed of an alkaline solution of organic reducing agents, the exposed silver halide crystals are reduced to metallic silver. The silver is dark in color and produces a negative image. The most commonly used developing agents are metol (p-methylaminophenol sulfate) and hydroquinone (p-dihydroxybenzene or 1,4-dihydroxybenzene).

The chemistry of development is complex. For example, hydroquinone in ordinary sulfite-containing developers (sodium sulfite is added to most developers as a preservative) is oxidized to a semi-quinone free radical, and then reacts with sulfite to form mono- and di-sulfonates. These reaction products may be isolated along with quinone, sodium sulfate (Na_2SO_4), and many other compounds associated with the other ingredients, e.g., metal, sodium carbonate, and potassium bromide.

If kept in the developer bath, even the unexposed silver halide crystals can be converted to metallic silver by the developer solution. To prevent this, the action of the developer is arrested by transferring the film to a stop bath. The stop bath is a weakly acidic solution (usually acetic acid) which neutralizes any of the alkaline developer carried over on the surface of the film or in the wetted gelatin layer. Following the stop bath, the film is immersed in a fixer solution that solubilizes and removes the remaining unreacted silver salts, rendering the image on the film permanent. Fixer solution adhering to the film must be removed in a final rinse step.

The film now contains a negative image of the scene which the camera recorded. A positive print is prepared by exposing a photosensitive sheet of paper to the image formed when light is passed through the negative image of the film. The paper is then processed through a similar set of operations (i.e., developer, stop bath, fixer, and rinse). A diagram for black-and-white processing that applies to both film and paper is shown in Figure 5.4.

Figure 5.4 Black-and-White Development Process



As more film is processed, the concentration of various reaction products gradually builds up in the developer solution. Silver and bromide ions removed from the developed film accumulate in the fixer solution, and the acidic stop bath is gradually neutralized as the quantity of alkaline developer carried over increases. At some point, these solutions become unusable and must be discarded. The final rinse is usually conducted in a continuous flow of fresh running water. As a result, only small amounts of silver and other fixer compounds can he detected in the spent rinse water waste stream.

Black-and-white reversal film processing, used to create a positive black-and-white image directly on the film, requires two development steps with an intermediate bleach step. Bleach solution for black-and-white processing contains sodium dichromate. Spent bleach is considered a hazardous waste because of its chrome content.

5.2 Manual and Automated Systems

5.2.1 Manual Systems

Manual systems include tray and tank processing. These are often used for low volume production such as black and white processing, enlargements, or other services that do not require, or are not amenable to, cost-effective automation. While manual processing wastes can be significantly reduced, this represents such a small volume for most businesses that the overall waste reduction impact may not be significant.

The tray method allows processing small quantities of film and papers with minimum chemical consumption. Sheets of film or paper are placed on the bottom of the shallow tray containing solution. The tray is then rocked back and forth manually to ensure that adequate fresh solution contacts the emulsion surfaces. The sheets are removed, drained, and transferred to the next processing bath. The duration of each step in the process is timed according to a prescribed schedule. Once the processing is completed, the solutions are returned to storage containers for reuse. With proper storage, solutions can be reused until chemically exhausted, as indicated by test strips.

Tanks are used for processing large quantities of film and paper sheets. This method is usually limited to sheets no larger than 8 inches by 10 inches. The sheets are suspended vertically in the tank from hangers which maintain a lateral separation. The solution level in each tank covers the entire sheet. The solution is agitated by gentle vertical movement of the hangers. When not in use, the tanks should be covered to keep foreign materials out of the processing solutions and to minimize evaporation and oxidation. Oxidation of the developer solution can be further reduced by using a tight-fitting "floating lid" of buoyant plastic and limiting the amount of time the solution is in use.

In addition, strips of camera film are often processed in tanks. The flexible film strip is inserted in a spiral slot in a reel which fits into a cylindrical tank. Inserting the film into the reel and loading the reel into the tank must be carried out in the dark. Then, in a lighted area, the solutions are added, one at a time, through a light-tight port in the cap. Following a prescribed schedule, the tank is drained and refilled with the subsequent solutions. During the final wash step, the cap can be removed to permit easier washing of the reels in the stream of water.(EPA 1991a)

5.2.2 Automated Systems

Automated systems differ primarily by the means used to transfer the film through the sequence of solutions. The major types of transport systems are discussed in the following paragraphs.(EPA 1991a)

Dip and Dunk. The films, in the form of sheets, strips, or short looped lengths, are clipped to hangers supported on a rack. The rack is removed from the processing machine to simplify loading. Once replaced in the processor, the rack holding the film is advanced by a gear chain mechanism. As the rack moves into position, it is lowered into the solution tanks so that the film is completely immersed. Agitation is provided by vertical movement of the rack to ensure continuous contact of the emulsion surface with fresh solution. As the rack continues its advance, it is automatically raised from one bath, allowed to drain, and lowered into the subsequent solution or wash tank. Finally the rack moves the film through a forced-air drying unit.

Nip Rollers. A series of small cylindrical wringers transports film or paper through the sequence of processing solutions. These rollers provide for both vertical and horizontal movement, and this method is suitable for either strips or sheets. Initially a leader strip or sheet is threaded and pulled through to a rewind station situated after the final dryer unit. Once the processing is started, movement of the film or paper through the solutions is continuous.

Belt Systems. The film or paper to be processed is supported on a belt which is conveyed through the sequence of solutions using guides and rollers. Where desirable, the material being processed can be transferred from one belt to another to allow for a greater variety of strips. Initially a leader strip or sheet is treated and pulled through to a rewind station situated after the final dryer unit. Once the processing is started, movement of the film or paper through the solutions is continuous.

High-Speed Roller. Long strips of film are mounted on a flexible support which is attached to a series of racks. A system of guides and immersed rollers conveys the film through the solutions to wash tanks. Before starting up the processor, a leader is threaded through the racks. Generally, the leader is attached to the end of the film and is always left in place between processing cycles to simplify start-up. Lengths of film to be processed, or tailing leaders, can be attached with tape or staples. High linear speeds are possible, resulting in greater throughput than can be obtained with other types of processors.

6. Water Use and Wastewater Sources and Characterization

6.1 Introduction

As exposed photosensitive film or paper is processed to develop the image, it is passed through a series of chemical baths and washes, as described in Chapter 5. In brief, the exposed film is first subjected to a reducing agent in the developer to form the latent image. Then, if the film being developed is color film, bleach is used to oxidize the black metallic silver image back to an invisible halide, so as to reveal the colors and so that the silver can be removed in the fix bath. Following, in the fix, ammonium or sodium thiosulfate solution is used to fix the silver or color image to the film base. In the ideal case, the fix solution removes 100 percent of the silver processed in color work, and the 60 to 80 percent of the silver in a black-and-white picture that does not contribute to the image as black elemental silver. Finally, one or more washes remove any remaining chemicals and unexposed silver. As film is passed through the developer, bleach, and fix, these solutions are replenished with new solutions to maintain their effectiveness. The rate of replenishment determines the particular wastestream amount and the concentration of chemicals in the wastestream.

Table 6.1 introduces the photoprocessing waste streams, their major constituents, and associated environmental concerns. Following are sections which detail the quantity and pollutant parameters of the major photoprocessing wastestreams: developer, bleach, fix, wash, and stabilizer.

Table 6.1 Aqueous Wastes from Photoprocessing

Solution	Constituents	Environmental Concern
Prehardeners, Hardeners, and Prebaths	Organic Chemicals Chromium Compounds	Oxygen Demand Toxic Metals
Developers	Organic Chemicals	Oxygen Demand
Stop Baths	Organic Chemicals	Oxygen Demand
Ferricyanide Bleaches	Ferricyanide	Toxic Chemical
Dichromate Bleaches	Organic Chemicals Chromium Compounds	Oxygen Demand Toxic Metals
Clearing Baths	Organic Chemicals	Oxygen Demand
Fixing Baths	Organic Chemicals Silver Thiocyanate Ammonium Compounds Sulfur Compounds	Oxygen Demand Toxic Metals Toxic Chemicals Ammonia Possible H_2S Generation
Neutralizers	Organic Chemicals	Oxygen Demand
Stabilizers	Phosphate	Bio-Nutrients
Sound-track Fixer or Redeveloper	Organic Chemical Ammonium Compounds	Oxygen Demand Ammonia
Monobaths	Organic Chemicals	Oxygen Demand

In addition, photoprocessing solutions may be acidic or alkaline.
Source: EPA 1991a

6.2 Total Process Water Use

Process water used in photoprocessing consists of a) film and paper wash water, b) solution make-up water, and c) area and equipment wash water. The largest single process water use is for the washing of film and paper between the various process steps and for final rinse. The function of the wash step is to clean the photographic emulsion of constituents which must be removed for successful completion of certain processing steps. Solution make-up water is blended with the chemicals used in the processing solutions, which are generally supplied to the processor in the form of liquid concentrates or powdered chemical formulations, to provide processing solutions of 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 is used for the washing and rinsing of solution mixing utensils, storage tanks, and processing machines for area washdown.

Information on overall process water use was obtained for a 1981 EPA guidance document for the control of water pollution in the photoprocessing industry.(EPA 1981a) The average total process water use for the 70 plants from which data were obtained was found to be 3.85 gallons per square foot of film and/or paper processed, and ranged from a low of 0.220 gal/ft^2 to a high of 14 gal/ft^2. It was observed that more than 95 percent of the process water use in each facility was for film and paper washing. The analysis also indicated that overall process water use was not correlated to production capacity; both small and large facilities showed a similar range.

The process volumes of silver-rich and silver-poor solutions have been estimated for a variety of small, medium, and large photoprocessors, as shown in Table 6.2. In this table, silver-rich solutions include fix, bleach-fix, washless stabilizer, and low-flow washwaters. Silver-poor solutions include developers, bleaches, stop-baths, stabilizers used after washes, and washwaters.

It is estimated that small and medium size photographic processors represent about 90% of the total number of photographic processing facilities. These small and medium size facilities include: small hospitals, doctors', dentists', veterinarians' and chiropractors' offices, neighborhood clinics, schools, portrait studios, minilabs, custom labs, professional processing labs, small microfilm facilities, printers, motion picture processors, and a large number of municipal, state, and federal facilities where some in-house photographic processing is done. Small facilities typically discharge less than 1,000 GPD of process wastewater and produce on average less than 2 GPD of silver-rich solutions. Medium size facilities typically discharge 1,000 to 10,000 GPD of process wastewater and produce on average 2 to 20 GPD of silver-rich processing solutions. Large photographic processors, representing about 9 percent of all photographic processing facilities, typically discharge 10,000 to 25,000 GPD of process wastewater and produce on average more than 20 GPD of silver-rich processing solution. Significant Industrial Users (SIU) are facilities using more than 25,000 gallons per day (GPD) of process wastewater and having the ability to adversely impact the POTW operations or causing pass-through of a regulated chemical. SIUs represent about 1 percent of the total number of facilities that process photographic materials. Photographic processing facilities that could be SIUs include the major motion picture film processors, and a few very large hospitals, X-ray diagnostic clinics, printers and photofinishers.(Silver CMP)

Photoprocessing combined wastestream characteristics are summarized in Table 6.3.

Table 6.2 Estimated Wastestream Volumes for Various Photoprocessors

Facility Type - Size	Silver-Rich[1] Solution Volume (GPD)	Silver-Poor[2] Solution Volume (GPD)
Dental Office - Small	0.1	5
Dental Office - Medium	0.2	10
Dental Office - Large	0.4	20
Hospital - Small	20	2,600
Hospital - Medium	40	5,200
Hospital - Large	80	10,400
Medical Professional - Small	0.2	100
Medical Professional - Medium	1.0	500
Medical Professional - Large	5	1,000
Microfilm - Small	0.1	15
Microfilm - Medium	0.3	75
Microfilm - Large	50	3,750
Printer/Graphic Art - Small	1	225
Printer/Graphic Art - Medium	2	450
Printer/Graphic Art - Large	20	4,500
Minilab - Washless - All Sizes	2.3	21
Minilab - Washwater - All Sizes	1.0	100
Photofinisher/Professional - Small	10	1,325
Photofinisher/Professional - Medium	100	13,250
Photofinisher/Professional - Large	265	33,000
Motion Picture - Small	25	1,000
Motion Picture - Medium	50	2,000
Motion Picture - Large	2,000	80,000
Police Dept. - Small	0.2	25
Police Dept. - Medium	0.4	50
Police Dept. - Large	2	250
School - Small	1	125
School - Medium	5	650
School - Large	10	1,250

[1] Silver-Rich solutions include fix, bleach-fix washless stabilizer, and low flow washwaters.

[2] Silver-poor solutions include developers, bleaches, stop-baths, stabilizers used after washes, and washwaters.

Source: Silver CMP

Table 6.3 Photoprocessing Combined Wastestream Effluent Characteristics

Pollutant Parameter	Concentration Range (mg/L)	
	Conventional Process	Washless Process
Temperature	80 - 110 °F	< 95 °F
pH	6.5 - 9.5 units	6.5 - 9.0 units
Biochemical Oxygen Demand (5-Day)	200 - 3,000	5,000 - 15,000
Chemical Oxygen Demand	400 - 5,000	10,000 - 35,000
Total Dissolved Solids	300 - 3,000	30,000 - 90,000
Total Suspended Solids	< 5 - 50	10 - 50
Ammonia Nitogen (NH_3-N)	20 - 300	6,000 - 10,000
Total Kjeldahl Nitrogen (TKN)	30 - 350	8,000 - 13,000
Thiosulfate	100 - 1,000	20,000 - 25,000
Sulfates	50 - 250	3,000 - 4,000
Silver (after silver recovery)	< 0.1 - 5	< 5 - 50
Iron	< 10 - 100	1,400 - 2,000
Zinc	< 0.75	< 2
Source: WEF 1994		

6.3 Developer

Developer replenishment rates typically range between 5 and 30 mL/sq ft for paper processes and 15 and 100 mL/sq ft for film processes.(WEF 1994, EPA 1981a) Fresh developer solutions typically contain less than 1 percent reducing agent by weight. For color developers, the reducing agent is a substituted para-phenylenediamine. The oxidized para-phenylenediamine formed during development reacts with another chemical to form the image dyes and remains in the gelatin layer. For black-and-white developers, the reducing agent is usually hydroquinone, a sulfonated hydroquinone, or ascorbic acid. The highest developing agent concentrations are found in some high-silver medical X-ray processes, for which the hydroquinone concentration can be as high as 3 percent by weight. In black-and-white processing, the oxidized developing agent remains in the developer solution.

The other major components of a developer solution consist of a pH buffer (typically carbonate) to maintain pH in the range of 9 to 11, a calcium sequestrant (typically ethylenediaminetetraacetic acid (EDTA) or a metaphosphate), and an antioxidant (typically sulfite or a hydroxylamine). These compounds are present in concentrations generally less than 1 percent by weight, in the 1 to 10 g/L range. Developer solutions contain more than 90 percent water by weight.

Because developing agents oxidize on exposure to air, the developing solutions are unstable and degrade with time. Thus the reducing agents are depleted by both the photoprocessing operation and by exposure to air. The oxidized ingredients must be replaced to maintain consistent results. As new solution is added to the developer container, an equivalent volume is discharged from the processor. This spent developer solution contains more than 90 percent water, with a few grams per liter inorganic salts (carbonate and sulfate) and portions of developing and sulfonated developing agents. Results of sampling of untreated color developer waste streams, performed in 1977, are displayed in Table 6.4.

Table 6.4 Color Developer Untreated Wastestream Pollutant Amounts

Pollutant Parameter	Plant Code	Concentration (mg/L)	Amount (lbs/1000 ft^2)
Total Organic Carbon	6208	6,450	-
	7781	15,000	-
	7781	16,700	-
Cadmium	6208	0.34	4.59×10^{-5}
	7781	86	3.5×10^{-3}
	7781	1.1	7.3×10^{-5}
Chromium*	6208	0.09	1.2×10^{-5}
	7781	0.10	4.1×10^{-6}
	7781	0.26	1.8×10^{-5}
Silver	6208	1.4	1.9×10^{-4}
	7781	1.5	6.1×10^{-5}
	7781	0.49	3.3×10^{-5}
Iron	6208	2.9	-
	7781	2.4	-
	7781	3.7	-
Lead	6208	0.25	-
	7781	7.5	-
	7781	0.09	-
Total Suspended Solids	6208	9.3	-
	7781	18	-
	7781	10	-
Total Dissolved Solids	6208	40,400	-
	7781	78,400	-
	7781	52,600	-

Source: EPA 1981a

* Since this sampling episode in 1977, it is reported that the amount of chromium used in film emulsion has been substantially reduced, and is currently used only in the Kodachrome process. (EPA 1994)

6.4 Bleach

Bleach replenishment rates vary from 5 and 30 mL/sq ft for color processes.(WEF 1994, EPA 1981a) Bleach solution is not used in black-and-white processing. Bleach solutions contain 10 to 30 percent iron-EDTA complex, typically the ammonium salt of ferric EDTA or ferric propylenediaminetetraacetic acid (PDTA). Ammonium salts are used because they are more soluble and transport through the gelatin layers faster than sodium or potassium salts. Thus, lower concentrations can be used. The bleach also contains 5 to 10 percent acetic acid and an acetate salt to buffer the pH in the 4 to 6 range, 5 to 10 percent bromide salt, and a small amount (less than l percent) of sodium or potassium nitrate, which is used to prevent corrosion of the processing tanks. As it oxidizes the metallic silver, the ferric complex is reduced to ferrous salt and must be regenerated or replaced. As this solution is replenished, the overflow will contain 65 to 85 percent water, ferrous and ferric EDTA or PDTA complexes, and inorganic salts such as bromide, nitrate, and ammonium ion.

For some cinemagraphic films, a bleach containing ferricyanide is used, and could result in appreciable concentrations of ferri- and ferrocyanide in the waste streams. Most cinemagraphic processors recover up to 99 percent of the ferricyanide for reuse. If not recovered, ferrocyanide can eventually be converted to free cyanide by sunlight in the presence of oxygen over a period of several weeks, and is therefore a waste constituent of concern.(EPA 1991a)

Results of sampling of raw EDTA bleach wastestreams, performed in 1977, are displayed in Table 6.5, and those of raw ferricyanide bleach wastestreams are displayed in Table 6.6.

Table 6.5 EDTA Bleach Untreated Wastestream Pollutant Amounts

Pollutant Parameter	Plant Code	Concentration (mg/L)	Amount (lbs/1000 ft^2)
Total Organic Carbon	2714	43,600	-
	4550	42,150	-
	7781	23,200	-
Cadmium	2714	< 0.02	$< 2.3 \times 10^{-6}$
	4550	0.4	1.4×10^{-4}
	7781	0.09	3.9×10^{-6}
Chromium*	2714	2.0	2.3×10^{-4}
	4550	12	4.2×10^{-3}
	7781	3.6	1.6×10^{-4}
Silver	2714	268	0.03
	4550	233	0.08
	7781	36	0.016
Iron	2714	16,282	-
	4550	12,102	-
	7781	7,722	-
Lead	2714	< 0.02	-
	4550	2.0	-
	7781	0.14	-
Total Suspended Solids	2714	62	-
	4550	112	-
	7781	86	-
Total Dissolved Solids	2714	253,000	-
	4550	227,600	-
	7781	206,800	-
Cyanide	2714	-	-
	4550	3.1	$1.1 \text{ X } 10^{-3}$
	7781	-	

Source: EPA 1981a

* Since this sampling episode in 1977, it is reported that the amount of chromium used in film emulsion has been substantially reduced, and is currently used only in the Kodachrome process. (EPA 1994)

Table 6.6 Ferricyanide Bleach Untreated Wastestream Pollutant Amounts

Pollutant Parameter	Plant Code	Concentration (mg/L)	Amount (lbs/1000 ft^2)
Total Organic Carbon	2714	13,000	-
	4550	30,750	-
	6208	8,300	-
Cadmium	2714	< 0.02	$< 1.1 \times 10^{-5}$
	4550	0.40	6.7×10^{-5}
	6208	< 0.02	$< 7.8 \times 10^{-7}$
Chromium*	2714	4.2	2.4×10^{-3}
	4550	1.3	2.2×10^{-4}
	6208	0.09	3.6×10^{-6}
Silver	2714	4.1	2.35×10^{-3}
	4550	8	1.3×10^{-3}
	6208	0.38	1.5×10^{-5}
Iron	2714	5,562	-
	4550	11,118	-
	6208	7,560	-
Lead	2714	0.22	-
	4550	2.0	-
	6208	0.42	-
Total Suspended Solids	2714	30	-
	4550	101	-
	6208	24	-
Total Dissolved Solids	2714	128,000	-
	4550	304,750	-
	6208	98,800	-
Cyanide	2714	15,800	9.1
	4550	50,200	20
	6208	14,750	4.75

Source: EPA 1981a

* Since this sampling episode in 1977, it is reported that the amount of chromium used in film emulsion has been substantially reduced, and is currently used only in the Kodachrome process. (EPA 1994)

6.5 Fix

Fix replenishment rates range from 15 to 100 mL/sq ft for film and paper processes. Fix solutions contain 65 to 85 percent water, 10 to 30 percent ammonium thiosulfate, and 5 to 10 percent sulfite salt that acts as an antioxidant. Fix solutions are not stable to oxygen, and exposure to air slowly degrades thiosulfate to elemental sulfur. As the fix solution is used for processing, it removes the silver from the film or paper in the form of the soluble silver thiosulfate complex, and a seasoned solution should contain between 1,000 and 5,000 mg/L silver. As the fix is replenished, the overflow is generally collected for silver recovery.(WEF 1994)

6.6 Bleach-Fix

As discussed in Chapter 5, the bleach and fix solutions necessary for color processing are sometimes combined to form the bleach-fix or blix solution. Bleach-fix replenishment rates vary from 5 to 30 mL/sq ft for color processes.(WEF 1994, EPA 1981a) The composition of the wastestream is that of the bleach and fix solutions, as described above, combined. Results of sampling of raw bleach-fix wastestreams, performed in 1977, are displayed in Table 6.7.

Table 6.7 Bleach-Fix Untreated Wastestream Pollutant Amounts

Pollutant Parameter	Plant Code	Concentration (mg/L)	Amount (lbs/1000 ft²)
Total Organic Carbon	2714	43,600	-
	4550	33,900	-
	4550	47,150	-
	7781	41,600	-
	7781	50,750	-
Cadmium	2714	< 0.02	$< 1.2 \times 10^{-6}$
	4550	< 0.06	$< 7.5 \times 10^{-5}$
	4550	1.0	6.6×10^{-5}
	7781	80	5.1×10^{-6}
	7781	0.24	1.6×10^{-6}
Chromium	2714	0.6	3.6×10^{-5}
	4550	5.7	7.1×10^{-4}
	4550	6	3.9×10^{-4}
	7781	1.3	8.2×10^{-5}
	7781	2.9	2.0×10^{-4}
Silver	2714	2,109	0.12
	4550	2,025	0.25
	4550	1,582	0.10
	7781	4,356	0.28
	7781	2,111	0.14
Iron	2714	4,884	-
	4550	7,718	-
	4550	8,023	-
	7781	5,310	-
	7781	13,236	-
Lead	2714	0.5	-
	4550	1.0	-
	4550	1.4	-
	7781	22	-
	7781	0.7	-
Total Suspended Solids	2714	112	-
	4550	56	-
	4550	82	-
	7781	124	-
	7781	51	-

Pollutant Parameter	Plant Code	Concentration (mg/L)	Amount (lbs/1000 ft^2)
Total Dissolved Solids	2714	205,000	-
	4550	195,400	-
	4550	209,400	-
	7781	292,000	-
	7781	306,200	-
Biological Oxygen Demand	2714	-	-
	4550	13,300	-
	4550	28,000	-
	7781	-	-
	7781	-	-
Nitrogen (As Ammonia)	2714	-	-
	4550	38,000	-
	4550	30,000	-
	7781	-	-
	7781	-	-
Source: EPA 1981a			

6.7 Wash

Wash waters are replenished at 200 to 1000 mL/sq ft for each wash tank of the process. After the fix or bleach-fix, the films or papers are immersed in a series of wash tanks to remove the silver thiosulfate and other residual chemicals from the gelatin layers. Therefore, the wash waters typically contain the same pollutants as the fix or bleach-fix, but at lower concentrations.

6.8 Stabilizers

Stabilizers or final rinse solutions are 99 percent water except for washless color processes. These solutions contain a wetting agent to prevent water spotting during drying. In some color film stabilizers, a small amount of formaldehyde (less than 0.2 percent) is present to harden the gelatin layer or stabilize an image dye. Stabilizers are replenished at rates between 10 and 30 mL/sq ft.

In one amateur film and paper process, the water washes are replaced by a replenished stabilizer. This stabilizer contains citrate salts and polyvinylpyrolidone to complex or react with the residual chemicals and provide image stability. As this solution is replenished, the overflow is collected for silver recovery. While the image stability is not as good as that provided by water washing, it is reportedly good enough for most amateur photographers.(WEF 1994)

6.9 Total National Photoprocessing Discharge Flow

Chapter 4 provides numbers for the total rolls processed and exposures produced, and provides information on the size and quantities of prints produced from the resulting negatives. From these values, and the surface area per film reported in the literature, it is possible to estimate the total square feet of film and paper processed across the United States for the amateur (commercial) market. Values for the health care and noncommercial photoprocessing market segments are not available, but it is estimated that this amateur market accounts for 44 percent of the total photoprocessing volume. This estimate derives from the fact that the amateur market accounts for 44 percent of total photographic silver use. Silver use in the other market segments, including medical, dental, graphic arts, and industrial, was shown previously in Table 4.3.

The detailed calculations, presented in the Appendix, estimate the total 1994 amateur film processed to be 296 million square feet, and the total paper processed to be 4,115 million square feet. From these results of the total film and paper square feet processed, the total flow requirements for each process can be calculated using the process flow demands for the various waste streams as reported in sections 6.2 through 6.7 above. The results are presented in Table 6.8 below.

Table 6.8 Total United States Photoprocessing Amateur MarketWaste Stream Quantity Estimations for 1994

Waste Stream	Flow Demands	Total U.S. Flow[1] (Millions of Gallons/Year)		
		Film	Paper	Film and Paper
Total Process[2]	3.85 gal/ft^2	-	-	17,000
Developer[3]	paper 5 - 30 mL/ft^2	-	19.0	-
	film 15 - 100 mL/ft^2	4.50	-	-
Bleach[3]	5 - 30 mL/ft^2	-	-	20.4
Fix[3]	15 - 100 mL/ft^2	-	-	67.0
Bleach-Fix[3]	5 - 30 mL/ft^2	-	-	20.4
Stabilizer[3]	10 - 30 mL/ft^2	-	-	23.3
Wash[3]	200 - 1000 mL/ft^2	-	-	699/tank
Total Process Calculated as: Developer + Bleach + Fix + Stabilizer + Three Wash Tanks				2,250

1. When given a flow demand range, the total U.S. flow is calculated using the average flow value.
2. Flow demand from reference EPA 1981a
3. Flow demands from reference WEF 1994

In Table 6.8 above, the total U.S. flow has been calculated in two ways: the single total process flow as determined from the EPA 1981a reference, or the addition of the process wastestreams as determined from the WEF 1994 reference. The EPA 1981a reference flow demand leads to a total flow about 7 ½ times greater than the flow calculated from the WEF 1994 flow demands. Here, the EPA 1981a value is taken to be outdated and to overstate water use, and the WEF 1994 values are taken to be more realistic for the current operating environment.

Two assumptions are implicit in the value of 2,250 million gallons/year as an estimate of the total U.S. photoprocessing flow requirements for the amateur market. One is that the flow demands which are not split for paper and film are applicable to both paper and film processing. The other is that other wastewaters not mentioned, such as equipment wash waters, are negligible.

7. Control and Treatment Technologies

7.1 Introduction

This chapter on control and treatment technologies recommended for photoprocessing operations begins with a discussion of source reduction methods. Particularly in the photoprocessing industry, certain management practices have proven highly effective in reducing waste while requiring almost no investment or loss in product quality. Following the discussion on source reduction, control and treatment technologies are presented. In addition to the environmental benefit associated with reducing pollutant discharge loadings, the photoprocessor is often at an economic advantage to install and maintain these technologies due to the payback from the recycled or recovered resources, especially with regard to the recovery of silver.

Photoprocessing equipment manufacturers and the photoprocessors have a close working relationship. Manufacturers supply processing systems which include both equipment and supplies to customers. Photoprocessors do not have to purchase chemical supplies from the same manufacturer that supplied the processing equipment, but many, especially the smaller mini-labs, often do. Processors rely heavily on manufacturers for compliance assistance and innovations to address environmental and regulatory concerns. Manufacturing is driven in part by the demands placed upon the processors, both by regulators and by the end consumer. For these reasons all of the manufacturers have support systems to assist the processors with operations and environmental compliance. Such systems include instructional seminars, facility compliance evaluations, and compliance kits. By keeping abreast of changes and implementing applicable technology improvements, companies can often take advantage of the dual benefits of reduced waste generation and a more cost efficient operation.

7.2 Source Reduction

The following management practices are applicable to all sizes of photoprocessing operations to minimize waste generation. They require almost no investment and have proven effective in many businesses:

- Control inventories of processing chemicals so they are used before their expiration dates.
- Make up processing solutions only in quantities needed to meet realistic processing volumes.
- Use floating lids or balls on developer solution tanks to prevent loss of potency through oxidation or evaporation.
- Improve quality control for all processes to prevent unnecessary discharges.(EPA 1991a)

Squeegees can be used in all manual and some automated processing systems to wipe excess liquid from the film and paper, reducing chemical carryover from one process bath to the next by 75 percent or more.(Kodak 1990) Several types are available, including wiper blades, air squeegees, vacuum squeegees, wringer sling squeegees, and rotary buffer squeegees. Belt turnarounds with soft-core rollers can be used for slow speed transport of wide films, but squeegees cannot be used on rack and tank, basket, or drum processors. Minimizing chemical contamination of process baths increases recyclability, enhances the life of the process baths, and reduces the amount of replenisher chemicals required. Some types of squeegees may damage the film image, if it has not fully hardened.

Accurately adding and monitoring chemical replenishment of the process baths will cut down chemical waste. Process baths may be protected from oxidation by reducing exposure to air. Some smaller photo developers store chemicals in closed plastic containers. Glass marbles are added to bring the liquid level to the brim each time liquid is used. This limits the volume of air in the container, thereby extending the chemical's useful life.

Proper storage conditions are necessary to maximize the life of paper for color prints. One writer recommends storing paper in a refrigerator, if it will not be used for a few days, and in a freezer for longer storage periods. He states that he has used the same box of paper for years by freezing it.(Sribnick)

Material substitution involves replacing a processing chemical with an alternate material that reduces the quantity of waste generated or the degree of hazard associated with the waste. Opportunities for this type of waste reduction in photoprocessing are limited. Alternate materials may be unavailable, more expensive, or have undesirable effects on product quality.

The "black box" nature of photoprocessing chemistry generally requires an individual operator to use established chemical packages with few options for substituting alternate materials. Photochemical manufacturers and suppliers can aid photoprocessors, however, by developing new processes which result in lower volume and lower toxicity wastes. For example, in most processes ferricyanide bleach has been replaced by ferric EDTA (ethylenediaminetetraacetic acid) complex, resulting in a less toxic waste stream.(Calif. DHSa)

Over the past 20 years, the industry has significantly reduced the content of silver in its products. The vast majority of silver in film is not used in the image and is recovered from processing solutions. However, the nature of the image formed determines the amount of silver used in that image; quality requirements for image and consistency limit the potential for further reduction.(EPA 1994)

As a result of the reduction in the silver content in film, the industry has also reduced the amount of hydroquinone in developer. There is a direct relationship between the amount of silver on the film base and the amount of hydroquinone required to develop the image. The amount of chromium used in the film emulsion has also been substantially reduced, and is currently used only in the Kodachrome process. The elimination of chromium in traditional films was primarily the result of regulatory demands on processors to eliminate it from their effluent. In contrast, the concern about selenium has arisen only recently with Xerox's development of a heat-based film which contains this element. Although Xerox is promoting the film on the basis of its silver-free nature, many in the industry claim that selenium is far more toxic than silver, and that from an environmental perspective, the new technology represents a step backward.(EPA 1994)

Businesses which operate in-house labs have more flexibility for material substitution, such as using non-silver film. A company that supplies microfilms of catalogs and standards to industrial users has switched to diazo and vesicular films. However, it should be noted that these films are not considered "archival" and may not be acceptable for permanent document storage.

7.3 Silver Recovery Considerations

Metallic silver trades as a commodity in units of Troy ounces (one Troy ounce equals 31.10 grams). In recent years the price range has typically been $4 to $6 per Troy ounce, although during the speculative fever of 1980, the price reached $50 per Troy ounce, before the market collapsed. Thus, if the market price were $6.00 per ounce, and an effluent contained 31 mg/L silver, the potential recovery value of silver would be 0.6 cents per liter or nearly 2.4 cents per gallon of effluent. Since silver recovered from photoprocessing requires further processing, reclaimers will offer somewhat less than market price for the recovered silver.(EPA 1991a)

The quantity of silver entering a processing facility can be estimated based on the number of rolls processed and the surface area of prints produced. The silver content in Troy ounces of several types of photographic films and papers, as well as the surface area per role of film, is available in EPA documents. While the silver content of film varies, the most commonly used films contain about 25 Troy ounces per 1000 square feet. Commonly used papers have about one tenth the silver content of film per square foot, at about 2.4 Troy ounces per 1000 square feet.(EPA 1991a, EPA 1991b)

Major sources of recoverable silver are: photoprocessing solutions, spent rinse water, scrap film, and scrap printing paper. The silver in these materials may exist as insoluble silver halide, soluble silver thiosulfate complex, silver ion, or elemental silver, depending on the type of process and the stage in the process where the silver is being recovered.

As much as 80 percent of the total silver processed for black-and-white positives and almost 100 percent of the silver processed in color work will end up in the fixer or bleach-fix solution. Silver is also present in the rinse water following the fixer or bleach-fix due to carry-over. The amount or silver in rinse water is only a small fraction of that in the fixer or bleach-fix solutions, but can be economically recovered when high volumes of rinse water are used. A variety of equipment types and sizes are available for silver recovery. Table 7.1 compares silver recovery methods. More detailed descriptions are given in Section 7.4 below.

Table 7.1 Comparison of Silver Recovery and Management Systems

System	Advantages	Limitations
Metallic Replacement by Chemical Recovery Cartridges (CRCs)	Can be used for all silver-rich solutions Little maintenance, low operating costs Low capital costs Simplest operation Can achieve 99% recovery when 2 CRC used in series	Requires metered flow for consistency Must be replaced on schedule Tendency to channel and cause concentrated silver discharge, efficiency diminishes with use High silver content in effluent unless 2 units in series Silver recovered as sludge High smelting and refining costs Cannot determine amount of silver recovered until refined pH dependent High iron content in effluent precludes reuse in photo process
Electrolytic (terminal)	High purity silver flake Low refining costs Can determine silver recovered Capital costs moderate Can achieve 90% recovery No additional chemicals released, fix solution can be recycled	Cannot achieve 5 mg/L with electrolytic alone Can sulfide if not properly maintained pH dependent Not suitable for silver-poor solutions
Precipitation	Can attain 0.1 mg Ag^+/L Little operator maintenance Low to moderate capital costs	Silver recovered as sludge Smelting costs higher than electrolytic Requires ongoing additives Complex operation Operation costs vary from moderate to high Potential H_2S release Treated solution cannot be reused Requires hazardous chemicals
Evaporation/ Distillation	Reduces wastes up to 90% Virtually zero overflow of silver	High energy requirements Moderate to high capital costs Silver recovered as a sludge Organic contamination buildup Concentration technology - Requires additional recovery
Reverse Osmosis	Efficiently recovers silver from dilute photoprocessing wastestreams Reduces effluent volume significantly No water treatment chemicals required Also recovers other chemicals Purified water is recyclable	Capital costs vary significantly Size of equipment needed to obtain sufficient flow Frequent maintenance of membrane and pumps Works best on dilute solutions such as washwater Large installations can be noisy Concentration technology - Requires additional recovery

System	Advantages	Limitations
Ion Exchange	Efficiently recovers silver from dilute photoprocessing wastestreams Can attain 0.1 - 2.0 mg Ag^+/L	Only for dilute effluent such as washwater Capital costs vary significantly Biological growth problems May require the use of hazardous chemicals Complex operation
Sources: Silver CMP, EPA 1991a, EPA 1994		

7.4 Silver Recovery from Fixer Solution

The most common methods of silver recovery from the fixer and bleach fix processing solutions are metal replacement, electrolytic recovery, and chemical precipitation. Ion exchange and reverse osmosis are other methods that can be used. However, these are suitable only for dilute silver solutions such as wash water from a primary silver recovery unit which has been mixed with wash waters. Some facilities use a primary silver recovery unit, which removes the bulk of silver, in combination with a "tailing" unit to treat the relatively low silver concentration effluents from a primary silver recovery system. Color developer effluent does not flow through a silver recovery unit because the silver content is very low and the high pH developer, if mixed with other silver-bearing solutions, could reduce the efficiency of silver recovery and could result in ammonia generation.(EPA 1991a)

A silver recovery system can be devoted to a single process line or can be used to remove silver from the combined fixer from several process lines in a plant. Multiple stream systems are more typical in large facilities. Sometimes a separate fixer system is used for specialty processing to reduce the possibility of inner-process contamination, which can occur when desilvered fixer is recycled to the photo process.

7.4.1 Metallic Replacement

Metallic replacement occurs when a more electrochemically active solid metal such as iron, contacts a solution containing dissolved ions of a less electrochemically active metal, such as silver. The more active metal goes into solution as an ion, being replaced by an atom of the less active metal in the solid matrix. The dissolved silver, which is present in the form of a thiosulfate complex, reacts with solid metal.

Silver ions will displace 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. Hypothetically, zinc and aluminum can also serve as replacement metals; however, both have drawbacks. Zinc is not used because of its relative toxicity and greater cost. Aluminum is not used because it simultaneously generates hydrogen gas, which can be an explosion and fire hazard if improperly handled.

Commercially available units consist of a steel wool-filled plastic canister with appropriate connections. These units are called chemical recovery cartridges (CRCs). Typical practice is to feed waste fixer to a train of two CRCs in series. The first CRC removes the bulk of the silver, and the second polishes the effluent of the first. It also is a safety factor if the first unit is overloaded. When the first is exhausted, the second becomes the first, and a fresh unit replaces the second. One supplier recommends changing CRC cartridges when the silver in the effluent of the first cartridge reaches 25 percent of the influent concentration.(Kodak 1980) The silver concentration in the effluent from a single cartridge averages 40 to 100 mg/L over the life of the system, versus a range of 0.1 to 50 mg/L when two CRCs are used in series. Fixer desilvered by this process cannot be recycled, because of excessive iron concentration in the effluent, which can average 4,000 mg/L.

For effective operation, the pH of the solution passing through the metallic replacement unit should be between 4 and 6.5. The optimum is between 5 and 5.5. Below pH 4, the dissolution of the steel wool is too rapid. Above pH 6.5, the replacement reactions may be so slow that silver removal is incomplete. Thus, proper pH control is important to high silver recovery. A CRC should recover about 85 percent of the recoverable silver in the form of a sludge, which must be further processed to produce pure metallic silver.(Calif. DHSa)

7.4.2 Electrolytic Recovery

An electrolytic unit can be used for a primary or a tailing waste stream, and can be either batch or continuous. This silver recovery method applies a direct current across two electrodes in a silver-bearing solution. Metallic silver deposits on the cathode. Sulfite and thiosulfate are oxidized at the anode:

$$H_2O + SO_3^{-2} \rightarrow SO_4^{-2} + 2e^- + 2H^+ \qquad \text{(Anode)}$$

$$SO_3^{-2} + S_2O_3^{-2} \rightarrow S_3O_6^{-2} + 2e^- \qquad \text{(Anode)}$$

$$Ag^+ + e^- \rightarrow Ag^0 \qquad \text{(Cathode)}$$

Approximately 1 gram of sodium sulfite is oxidized for each gram of silver deposited. Considerable agitation and large plating surface areas can achieve good plating efficiency and silver up to 90-98 percent pure. Lower silver purity levels usually result from tailing unit applications because of the lower silver concentration in the influent solution. The cathodes are removed periodically, and the silver metal is stripped off. An electrolytic system should recover about 90 percent of the recoverable silver.

Care must be taken to control the current density in the cell because high density can cause "sulfiding." Sulfiding is the decomposition of thiosulfate into sulfide at the cathode which contaminates the deposited silver and reduces recovery efficiency. The higher the silver concentration, the higher the current density can be without sulfiding. Therefore, as the silver is plated out of solution, the current density must be reduced.

7.4.3 Batch Electrolytic Recovery

In batch recovery, overflow fixer from one or more process lines is collected in a tank. When sufficient volume is reached, the waste fixer is pumped to an electrolytic cell for silver removal. The desilvered fixer can be discharged to a sewer, disposed of as solid waste, or reused. If reused, it is transferred to a mix tank where sodium thiosulfate is added to replenish its strength.

Primary batch system cells are usually designed to desilver the fixing batch at initial silver concentrations of about 5,000 mg/L. The silver concentration in the effluent is typically 200 to 500 mg/L. Effluent of 20 to 50 mg/L is possible with additional treatment time and careful current density control. An electrolytic tailing cell typically achieves the lower range because the process can be optimized for low initial silver concentrations.

7.4.4 Continuous Electrolytic Recovery

The volume of a continuous electrolytic unit must be large enough relative to the incoming flow volume to ensure adequate residence time of the fixer, so two or more units can be placed in series to achieve this. The continuous flow of incoming fixer supplies a constant quantity of silver for electrolytic recovery. As a result, the units can be operated at a relatively stable current density. Such systems can be automatic. Some units can sense silver concentration in solution and adjust current densities. Usually, continuous flow units discharge desilvered fixer directly to the sewer.

7.4.5 Recirculating Electrolytic Recovery

Silver can also be removed from an in-use fixer solution at approximately the same rate it is added by film processing, using a continuously recirculating system. The recovery cell is connected "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 fixer processing solution, which minimizes the amount of silver carried out into the wash tank. Also, the fixer replenishment rate is reduced, decreasing chemical usage and discharge quantities. The silver concentration in the fixer can be maintained in the range of 500 to 1,000 mg/L without forming sulfide.

A recirculating silver recovery unit receives a small continuous stream of fixer from an in-use process tank, removes the silver, then returns the desilvered fixer to the photoprocessor.

Each photoprocessing unit requires a separate silver recovery unit. Systems are available for treating all types of non-bleach fixers that have circulation pumps. Once installed, the unit is fully automatic, turning itself on by sensing the flow of fixer through the electrolytic cells. The cells themselves contain no moving parts, and the silver is harvested every two to three months.

Desilvered fixer solution can be reused, whether from an "in-line" continuous system or from batch. This requires adequate monitoring and process control to maintain composition and protect quality. Some manufacturers have special electrolytic fixers for this application. Parameters (pH, silver, and sulfate concentrations) should be monitored to maintain the physical and chemical properties of the fixer solution, usually through the addition of make-up chemicals.

7.4.6 Chemical Precipitation

Chemical precipitation is the oldest and cheapest method for recovery of silver. It is widely used by manufacturers of photographic supplies but usually not by photoprocessors. The two primary disadvantages are that extremely toxic hydrogen sulfide gas (H_2S) can be evolved, and that the resulting sludge may have to be managed as a hazardous waste. A third disadvantage is that recovery of silver from the sludge is more difficult than with other methods.

Sodium sulfide (Na_2S) causes silver sulfide to precipitate readily from waste fixer solutions.

$$2Ag^+ + S^{-2} \rightarrow Ag_2S$$

Silver sulfide is extremely insoluble with a solubility product of 10^{-50}. Precipitation must be carried out in alkaline media to avoid the generation of H_2S. Silver sulfide tends to form colloidal suspensions. Its very small particle size makes filtration difficult, and the filter cake generated is extremely dense. However, diatomaceous earth filter aid can be used to improve filtration. About three grams filter aid are required for each gram of silver, if a conventional plate-and-frame filter press is used.(Calif. DHSa)

Sodium borohydride ($NaBH_4$) is also an effective precipitant for silver:

$$NaBH_4 \rightarrow Na^+ + BH_4$$

$$BH_4 + 2H_2O + 8Ag^+ \rightarrow 8Ag^0 + 8H^+ + BO_2$$

The borohydride method requires significantly more than the stoichiometric quantity to complete the reaction, while sodium sulfide precipitation requires use of very little excess chemicals. Borohydride also reduces many other metals such as cadmium, lead, and mercury.(Cook) The major difference between the two processes is the resulting silver quality. Sodium borohydride produces elemental silver of 96 to 98 percent purity. Either method can reduce silver concentrations to 0.1 mg/L in the fixer waste water.

The process mixes the precipitation agent with the silver bearing wastewater in a batch reaction tank equipped with automatic pH control. When sodium sulfide is used, the pH must be maintained above 7 to avoid releasing H_2S. The optimum pH range for sodium borohydride precipitation is 5.5 to 6.5. Solid particles having a size of 1 to 2 microns are formed, and are allowed to settle before filtering. Usually solutions reacted with either sodium sulfide or sodium borohydride are not reused in the photographic process.

7.5 Silver Recovery from Rinse Water

Even with an efficient fixer solution silver recovery system and an effective squeegee on the fixer tank, up to 10 percent of the recoverable silver is lost by carry-over into the rinse tank. The silver concentration in the spent rinse water is typically in the range of 1 to 50 mg/L, too low for economical recovery with electrolytic or metallic replacement methods. In addition, the iron by-product from metallic replacement precludes reuse of the rinse water, although some photoprocessors use metallic replacement to meet municipal sewer effluent limits. Precipitation is uneconomical for rinse water.(Calif. DHSa)

Two methods are currently being used for effective recovery of silver from rinse water: resin ion exchange and reverse osmosis (RO). A third method, called "low flow prewash," has been used in a few locations in the United States.

7.5.1 Ion Exchange

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

$$\text{(Resin)-Cl} + AgS_2O_3^- \rightarrow \text{(Resin)-}AgS_2O_3 + Cl^-$$

The silver-thiosulfate complex has a high affinity for the resin, making it difficult to reclaim the silver and regenerate the resin. Other problems include plugging of the resin by suspended matter, such as gelatin, but these have also been solved by improved equipment design and operational procedures. Some ion exchange units produce effluents with silver concentrations as low as 0.1 ppm, recovering as much as 98 percent of the silver.(Kodak 1990) High-capacity units can process as much as 500 gallons per hour.(Calif. DHSb)

7.5.2 Reverse Osmosis

In reverse osmosis (RO) techniques, the waste water stream flows under pressure over the surface of a selectively permeable membrane. Water molecules pass through the membrane and other constituents are left behind. The extent of separation is determined by membrane surface chemistry and pore size, fluid pressure, and waste water characteristics. The RO unit has one inlet to receive the waste stream, and two discharge outlets. Purified water (permeate) exits from one outlet, and concentrated wastewater exits from the other. This process reportedly can recover 90 percent of the silver thiosulfate.(Kodak 1990) Silver can be recovered from the resulting concentrate by conventional silver recovery methods. The wastewater must be pumped to high pressure (about 600 psig) before feeding the RO unit, which may incur high energy and maintenance costs. Operating problems include fouling of the membrane and biological growth. Proper maintenance and control can alleviate these problems. One plant reported membrane fouling, which required frequent membrane replacement at high cost. The problem was solved by installing a sandbed filter upstream of the RO unit.(Calif. DHSa) RO requires more capital investment than most other silver recovery methods, discouraging its use in photoprocessing. (Kodak 1990)

7.5.2 Low Flow Prewash

Low flow prewash involves segmenting the after-fix wash tank to perform the washing in two stages, with separate rinse water make-up and overflow. It does the after-fix washing in two stages. Most of the silver carry-over is washed off in the low volume, after-fix prewash tank. The system lessens dilution of the silver carry-over, but means that concentrations of fixer, silver, and other chemicals reach high levels in the prewash tank under steady-state conditions. One problem is that the work being processed may receive additional fix time and exposure to concentrated contaminants while immersed in the prewash. Some investigators fear that this may harm the quality of the processed material. Dye stability tests on color paper processed using the prewash system showed an increase in yellow stain six months after processing. Another problem is increased maintenance of the wash tank because of biological growth, although this can be controlled with biocides.(Calif. DHSa)

7.5.4 Silver Recovery from Scrap

Scrap film and paper result from trimmings, test strips, and leaders. The silver may be present in the form of silver salts or elemental silver from fogged or developed material. The processing of solid materials is more cumbersome than for solutions, but there are a number of silver recovery companies in business that will buy solid scrap. If necessary, the silver in scrap film and paper can be removed in the photo lab by treating the material with a sodium hypochlorite solution to oxidize elemental silver, assuring that all silver is in the form of salts that can be removed by fixing. Some photo labs collect fixer overflow in a container and add unprocessed scrap film or paper as it is generated. Once dissolved in the fixer, the silver can be recovered through the same silver recovery processes used by the lab for the fixer solutions from the photoprocessors. This approach can increase the amount of silver recovered on site, but can also be a bit messy. Digested film or paper can be difficult to handle and may even go sour, if left in the container long enough to be attacked by bacteria.(Calif. DHSa)

Processed or unprocessed film can be soaked in an agitated, hot solution of sodium hydroxide to remove the emulsion. The silver can then be separated from the solution by settling, centrifuging or filtering. If the film base is to be sold as scrap polymer after the silver bearing emulsion has been removed, the film is segregated by type of base.

7.6 Color Developer Reuse

Color developers which can be regenerated are available, allowing the photoprocessor to reduce replenisher purchases about 50 percent. One regeneration process requires the addition of an ion-exchange unit to remove the excess development by-products from the developer overflow. Another process accomplishes the same objective without ion exchange, using a different developer solution.(Kodak 1989a)

7.7 Ferricyanide Recovery

Ferricyanide bleaches reduce to ferrocyanide during the bleach process. The spent ferrocyanide can be regenerated either electrolytically or chemically. Chemical methods employ either ozone or persulfate. Regenerated ferricyanide can be re-used in photoprocessing.

7.7.1 Electrolytic Regeneration

Spent bleach is fed to an electrolytic cell, where the following reactions occur:

Anode: Primary: $2Fe(CN)_6^{-4} \rightarrow 2Fe(CN)_6^{-3} + 2e^-$
Secondary: $4OH^- \rightarrow O_2 + H_2 + 2OH^- + 2e^-$

Cathode: Primary: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Secondary: $Fe(CN)_6^{-3} + e^- \rightarrow 2Fe(CN)_6^{-4}$

The evolution of hydrogen gas presents a potential safety hazard.(Kodak 1990)

7.7.2 Persulfate Regeneration

This method is relatively inexpensive and safe, since it does not liberate any hazardous gases. The reaction is:

$$2Fe(CN)_6^{-4} + S_2O_8^{-2} \rightarrow 2Fe(CN)_6^{-3} + 2SO_4^{-2}$$

The major disadvantage is that gradual accumulation of sulfate salt reduces bleaching efficiency.(Kodak 1990)

7.7.3 Ozone Regeneration

Ozone reacts with ferrocyanide to form ferricyanide as follows:

$$2Fe(CN)_6^{-4} + O_3 + H_2O \rightarrow 2Fe(CN)_6^{-3} + 2OH^- + O_2$$

Hydrobromic acid is also added to control pH and to supply the bromide ion needed for the bleach process. The major advantage of this process is that there is no salt buildup. Disadvantages include high initial cost for the ozone generator and potential safety problems, since ozone is corrosive, unstable, and high reactive. Because of these disadvantages, this process is likely to be used only by large labs.(Kodak 1990)

7.7.4 Ion Exchange

Bleach water containing dilute concentrations of hexacyanoferrates (either ferricyanide or ferrocyanide) can be passed through a column containing a weak base anion exchange resin, which removes the hexacyanoferrate. The resins is then regenerated with sodium hydroxide, and the recovered hexacyanoferrate reacted with ozone or persulfate to recover ferricyanide as shown above. Treated effluent from this process can contain as little as 0.075 mg/L (75 parts per billion) hexacyanoferrate.(Kodak 1990)

7.7.5 Reverse Osmosis

Reverse osmosis can remove up to 95 percent of the salts from fixer solutions, including nearly all of the hexacyanoferrates. The capital investment is relatively high, which has limited applicability of this process in photoprocessing.(Kodak 1990)

7.7.6 Precipitation

Fixer overflow can be treated with ferrous sulfate and a flocculent to produce ferrous ferrocyanide. Then either sodium or potassium hydroxide is added to make the ferrocyanide, which can be reoxidized with one of the bleach regeneration techniques. The resulting ferricyanide can be reused as bleach replenisher.

Another method uses calcium chloride to precipitate the salt $Ca(NH_4)_2Fe(CN)_6$. This method can reduce ferrocyanide concentration of some color-reversal fixers to less than 1 g/L. (Kodak 1990)

7.8 Rinse Water Use: Reduction and Recycling

To maintain product quality, many photoprocessing operations use continuous rinse water flows. The result is rinse water waste streams usually are the highest volumes of waste from photoprocessors. This effluent consists primarily of water with low concentrations of chemicals from the carry-over of the processing solutions. Commercial rinse water recycling systems are available for photoprocessing operations. Spent rinse water can be treated to restore purity and recycled for rinsing. A small portion of incoming clean water is added to the recycled water stream, and an equivalent overflow goes to the sewer drain after the fixer wash. A single recycling system can serve several photoprocessor units.

Water conservation is important in certain parts of the United States where either (a) fresh water is in short supply or (b) local regulations severely limit or prohibit discharge of photoprocessing effluents to the sewer system. Some operators simply shut off the rinse water except when film is moving through the processor. However, certain processors require a continuous water flow to maintain temperature control. Many locales have established concentration-based limits on aqueous effluents, which encourages greater rinse water use for dilution. Photoprocessors must check the local requirements to be sure that reducing water without proportionately reducing all other contaminants will not violate the concentration limit.

7.8.1 Countercurrent Rinsing

Continuous photoprocessing trains may employ a series of rinse steps, designed so that water flows countercurrent to the process. Thus, fresh water is fed to the final stage. Overflow water then goes to the next stage upstream. Of course, the rinse water becomes more contaminated in each succeeding stage. Thus, it may be economical to use squeegees to minimize carryover of contaminants into each rinse stage, and a squeegee between the processing solution and the first wash stage is recommended. Otherwise, efficiency will be impaired and product quality will degrade.

7.8.2 Plumbingless Minilabs

Plumbingless minilabs use a proprietary chemical stabilizer in place of wash water. While conventional minilabs discharge 20 to 25 gallons of effluent per roll of film processed, this type of lab discharges less than 0.1 gallon of effluent per roll. Although the volume of effluent is greatly reduced, the concentrations of contaminants are much higher than for conventional minilabs. Wherever there are concentration limits on sewer discharges, potential users should review this point with local authorities if silver can be recovered from this effluent using either the metallic replacement or electrolytic processes described above.(Kodak 1989b)

7.8.3 Evaporation

Another option in managing waste photographic solutions is evaporation, in which the wastewaters are collected and heated to evaporate all liquids. This is often done under vacuum to reduce the boiling temperature. As the water and volatile compounds are removed, soluble materials remain to form a sludge. The sludge is collected in filter bags, which can be sent to a silver reclaimer for recovery. Evaporation can accommodate operations that do not have access to sewer connections or waste water discharge. If the water vapor is condensed and recycled, instead of being vented to the atmosphere, then this can be considered a source reduction technique.

One manufacturer has an automatic recirculating system in which aqueous effluent is continuously introduced into the evaporation chamber. The water is vaporized, then condensed and recycled to a rinse water holding tank. As the water evaporates, the solids are collected in one of two 5-micron filter bags. When the unit senses that the filter bag is full, it switches the flow to the other filter bag, and alerts the operator to remove the filled bag.

The advantage of this approach is it achieves "zero" water discharge. Virtually all of the silver in the waste solutions is captured with the solids. There are several disadvantages, however. One is that volatile organics in the waste solution may be evaporated as well, creating an air pollution problem. One evaporation unit has a charcoal air filter to capture these organics.

A second disadvantage is that any organics which condense with the water will be recycled also, causing a potential buildup of their concentrations in the process. Finally, this is an energy intensive technique and so carries associated high energy costs and fuel-use environmental effects. (Calif. DHSa)

7.9 Implementation of Control Technologies

As detailed above, photoprocessors practice chemical recovery and wastewater treatment for both economical and environmental reasons. The wastewater from photoprocessing operations has been a focus of regulation because of a number of parameters, including toxic metals, toxic chemicals, oxygen demand, ammonia, and bionutrients. Table 7.2 below presents 1991 data on the use of environmental controls and chemical recovery methods by commercial photoprocessors.

Table 7.3 summarizes the silver concentration at typical recovery efficiencies for end of process, in combination with low silver solutions, and in combination with process wash waters.

Table 7.2 Commercial Photoprocessor Environmental Controls, 1991

	All Specialty Retailers Combined	Camera Store with Minilab	Stand-Alone Minilab	Mail Order, Wholesale, and Captive Labs	Portrait Studio Firms
Percent Operating Silver Recovery Systems		96.3%	89.5%	100%	66.7%
Type of Silver Recovery System Used:					
• electrolytic recovery	80.7%	82.6%	81.0%	94.7%	63.2%
• steel-wool canister	45.8%	48.9%	43.9%	57.9%	36.8%
• ion exchange	3.6%	0.9%	6.3%	20.8%	2.0%
• evaporation/distillation	2.4%	0.9%	0.3%	8.3%	4.1%
Percent that Recycle Water	7.8%	10.2%	7.2%	40.9%	10.0%
Percent that Regenerate Chemistry	25.8%	19.6%	28.6%	86.4%	22.6%
Percent of Firms Visited or Contacted by State or Local Water Authority in 1991		13.1%	25.4%	73.3%	25.0%

Source: EPA 1994
Note: Population basis for these values was unspecified in source report (EPA 1994).

Table 7.3 Silver Concentrations After Silver Recovery (mg/L)

Percent Recovery	Ag in Silver-Rich After Recovery[1]	When Combined with Silver-Poor[2]	When Combined with Wash Water[3]
90%	200 - 800	100 - 400	10 - 40
95%	100 - 400	50 - 200	5 - 20
99%	20 - 80	10 - 40	1 - 4
99.9%	2 - 8	1 - 4	0.1 - 0.4

Source: Silver CMP

1. Silver concentrations after recovery.

2. Silver concentrations when treated silver-rich solutions are combined with silver-poor solutions. Silver-rich solutions include fix, bleach-fix, washless stabilizer, and low-flow washwaters. Silver-poor solutions include developers, bleaches, stop-baths, stabilizers used after washes, and washwaters.

3. Silver concentrations when treated silver-rich solutions are combined with silver-poor solutions and process washwaters.

7.10 Control and Treatment Issues

A barrier to the effective treatment of photoprocessing wastewaters is the small size and lack of technical sophistication of many of the photoprocessors. Processes to remove silver and other pollutants from wastewaters require careful operation and maintenance to achieve their design effectiveness. Many photoprocessors, especially the minilabs within drug stores, grocery stores, and department stores, do not have staff with sufficient training and longevity to operate this equipment effectively.(EPA 1994)

High prices for certain inputs have encouraged reduced use of those inputs over time. In addition competition based on product quality has encouraged some environmental improvements. This congruence between economic and environmental goals was particularly noted with respect to silver. Past increases in the price of silver encouraged efforts both to reduce the amount of silver used in sensitized products and to increase silver recovery and recycling. The extent to which silver is recycled is sensitive to price, and according to industry participants is currently hampered by the combination of moderate prices for silver and the costs of complying with RCRA rules. However, actions taken to reduce the amount of silver in sensitized products also had the effect of improving product quality. According to industry contacts, competition based on product quality has continued to encourage the use of less silver over time, independent of fluctuations in the price of silver.(EPA 1994)

The high cost of replacing photoprocessing equipment acts as an economic barrier to improved environmental performance. Many environmental improvements (e.g., processes that recycle photoprocessing chemicals) are embedded in the photoprocessing equipment, and replacement of existing equipment is required to achieve those improvements. Photoprocessors are reluctant to replace equipment before the end of its useful life, especially minilabs, for whom the capital investment can be a substantial burden. While the equipment replacement cycle acts as some constraint on the speed of environmental improvements, it is not clear that is causes significant delays. The basic pace of product and process improvements results in a turnover of photoprocessing equipment in only eight years on average, according to industry experts.(EPA 1994)

Photographic product users' needs are also cited by industry contacts as a factor influencing the pace and extent of environmental improvements. As described earlier, different end-use segments present different demands that influence the nature of the leading photoprocessing chemistry over time. For example, the market demand for one-hour processing eliminates many opportunities for reducing the chemical content of processing packages. If chemicals are reduced, the film must remain in the solution longer, extending the time required for developing. Also, the accuracy an quality requirements of x-ray film an graphic arts film limit the potential for alternatives to silver-halide-based film.(EPA 1994)

8. Environmental Assessment

8.1 Introduction

This chapter examines the effects that the pollutants discharged from the photoprocessing industry may have on human health, aquatic ecosystems, and Publicly Owned Treatment Works (POTWs). First, the list of characteristic photoprocessing pollutants, introduced in Chapter 6, is re-examined. Next, pollutant loads as reported in the national Permit Compliance System (PCS) database are presented. Total industry pollutant loads are then calculated using estimated flows and pollutant concentrations from Chapter 6. A toxic weighting factor analysis is performed for the list of characteristic pollutants. This analysis is used to show the relative toxicity of the effluent components in a manner consistent with the effluent guidelines program. These toxic weighting factors are used in conjunction with the calculated pollutant loads to estimate industry-wide toxic loads.

Next, a qualitative, pollutant-by-pollutant list of potential environmental impacts and fate is presented for typical photoprocessing effluent constituents. Evidence in the scientific literature of the negative environmental effects of photoprocessing wastewater is summarized. The three areas of concern explored here include impacts on activated sludge treatment, impacts on human health, and impacts on aquatic ecosystems.

A separate section is devoted to the potential impacts and speciation of silver, which is the pollutant of greatest concern in photoprocessing effluent. It is explained that, although certain ionic forms of silver are considerably toxic, especially to aquatic invertebrates, more prevalent compound and complexed forms of silver are generally less toxic.

8.2 Pollutants Found in Photoprocessing Effluent

Table 8.1 lists the main pollutants mentioned in Chapter 6 as possible photoprocessing wastewater constituents. Two of the pollutant parameters (Temperature and pH) are not pollutants in the traditional sense and will not be discussed further here. Five (COD, BOD, TSS, TKN and TDS) are classes of pollutants and not individual pollutants. Discussion of health effects, environmental effects, and POTW treatment for many of these pollutants follows the loading analysis in Section 8.4. For other parameters, health and environmental effects and POTW removal data were not available.

Table 8.1 Possible Photoprocessing Wastewater Constituents

Pollutant Parameter	
Ferri- and Ferro-cyanide	Temperature
Cyanide	pH
Chromium	Biochemical Oxygen Demand (BOD)*
Para-phenylenediamene	Chemical Oxygen Demand (COD)*
Hydroquinone	Total Dissolved Solids (TDS)*
Sulfonated Hydroquinone	Total Suspended Solids (TSS)*
Ascorbic Acid	Ammonia Nitrogen (NH_3-N)*
Ethylenediaminetetraacetic acid (EDTA)	Total Kjeldahl Nitrogen (TKN)*
Hydroxylamine	Thiosulfate*
Iron-EDTA Complex	Sulfates*
Propylenediaminetetraacetic acid (PDTA)	Silver (after silver recovery)*
Ammonia Thiosulfate	Iron*
Silver Thiosulfate	Zinc*

* Pollutants for which data are available to calculate total annual discharge loads

Another source for pollutant information for the photoprocessing industry is the Permit Compliance System (PCS). PCS is a computerized information management system maintained by EPA's Office of Enforcement and Compliance Assistance (OECA). PCS contains data on permit conditions and monitoring, compliance, and enforcement for facilities with National Pollutant Discharge Elimination System (NPDES) permits. NPDES permits are applicable only to facilities that discharge directly to surface waters. However, some states also include data from facilities that discharge to groundwater in the PCS data base, so these groundwater data are also available in the PCS data base. Among other items, PCS records indicate the pollutant parameters listed in the permit, and may also contain information of the loadings of these pollutants discharged in the facility's wastewater.

Only five facilities in the United States are currently permitted and listed in the PCS data base under the photoprocessing SIC codes. The pollutants and limits in these permits are based on ground water controls or water quality load allocations: none are based on Subpart A of 40 CFR Part 459. Table 8.2 summarizes the pollutants and annual loadings for these facilities for 1995. Loadings for Facilities 1, 2, 3, and 5 are all to groundwater. Facility 4 discharges its wastewaters directly to surface water.

Table 8.2 Pollutant Loadings for Direct Discharge Photoprocessing Facilities, 1995

Units are pounds per year, except flow is in gallons per year.
"Not Mon." indicates that pollutant was not monitored in the permit.

Pollutant	Facility 1	Facility 2	Facility 3	Facility 4	Facility 5
Flow (gallons/yr)	1284	12090	45210	33,480,000	201,000
Fluoride, Total (lbs/yr)	0.004394	Not Mon.	0.053113	Not Mon.	Not Mon.
Copper, Total	0.001479	0.035028	0.032011	Not Mon.	Not Mon.
Iron, Total	0.000589	0.660947	0.058013	Not Mon.	0.397
Nickel, Total	0.005958	Not Mon.	Not Mon.	Not Mon.	Not Mon.
Silver, Total	0	0.001382	0.014938	Not Mon.	0.044
Zinc, Total	0.009923	Not Mon.	0.050807	Not Mon.	Not Mon.
Foaming Agents	0	Not Mon.	0.04808	Not Mon.	Not Mon.
Nitrogen, Total	Not Mon.	0.32509	Not Mon.	Not Mon.	3.925
Lead, Total	Not Mon.	0.001888	Not Mon.	Not Mon.	Not Mon.
Phenolics, Total Recov.	Not Mon.	0	Not Mon.	Not Mon.	0
Methylene Chloride	Not Mon.	0	Not Mon.	Not Mon.	Not Mon.
Oil & Grease	Not Mon.	Not Mon.	1.029303	0	Not Mon.
Nitrate, Total as N	Not Mon.	Not Mon.	1.444289	Not Mon.	Not Mon.
Magnesium, Total	Not Mon.	Not Mon.	3.475618	Not Mon.	Not Mon.
Sulfate, Total	Not Mon.	Not Mon.	15.86418	Not Mon.	Not Mon.
Iron & Manganese, Total	Not Mon.	Not Mon.	0.061863	Not Mon.	Not Mon.
Boron, Total	Not Mon.	Not Mon.	0.061142	Not Mon.	Not Mon.
Chromium, Total	Not Mon.	Not Mon.	0.002772	Not Mon.	Not Mon.
Manganese, Total	Not Mon.	Not Mon.	0.002772	Not Mon.	Not Mon.
Antimony, Total	Not Mon.	Not Mon.	0.004927	Not Mon.	Not Mon.

Pollutant	Facility 1	Facility 2	Facility 3	Facility 4	Facility 5
Aluminum, Total	Not Mon.	Not Mon.	0.030341	Not Mon.	Not Mon.
Nitrogen- NH_3 as NH_3	Not Mon.	Not Mon.	0.948351	Not Mon.	Not Mon.
Phenolic Compounds	Not Mon.	Not Mon.	0.003318	Not Mon.	Not Mon.
Solids, Total Dissolved	Not Mon.	Not Mon.	115.4557	131328.1	Not Mon.
Bromide	Not Mon.	Not Mon.	0.303408	Not Mon.	Not Mon.
BOD, 5 day	Not Mon.	Not Mon.	Not Mon.	1397.108	Not Mon.
Solids, Total Suspended	Not Mon.	Not Mon.	Not Mon.	1229.455	Not Mon.
Nitrogen - NH_3 as N	Not Mon.	Not Mon.	Not Mon.	22.0743	Not Mon.
Cyanide, Total	Not Mon.	Not Mon.	Not Mon.	5.588431	0.044
Silver, Dissolved	Not Mon.	Not Mon.	Not Mon.	0.055884	Not Mon.
Silver, Total Recoverable	Not Mon.	Not Mon.	Not Mon.	0.111769	Not Mon.
Zinc, Total Recoverable	Not Mon.	Not Mon.	Not Mon.	2.794216	Not Mon.
Aluminum, Total Recoverable	Not Mon.	Not Mon.	Not Mon.	27.67218	Not Mon.
Aluminum, Dissolved	Not Mon.	Not Mon.	Not Mon.	27.94216	Not Mon.
Cadmium, Total Recoverable	Not Mon.	Not Mon.	Not Mon.	2.794216	Not Mon.
Chromium, Total Recoverable	Not Mon.	Not Mon.	Not Mon.	2.794216	Not Mon.
Chlorine, Total Residual	Not Mon.	Not Mon.	Not Mon.	27.94216	Not Mon.
COD	Not Mon.	Not Mon.	Not Mon.	10897.44	Not Mon.
Acetone	Not Mon.	Not Mon.	Not Mon.	Not Mon.	0.022

This table shows that there is a wide disparity in the pollutants measured (permitted) from facility to facility. The variation of these photoprocessing pollutant parameters is a subject for future investigation. Permit writers also have chosen to require measurement of certain parameters (for example, silver) by different means (total silver, dissolved silver, and total recoverable silver) at different facilities. The reported loads for most parameters other than conventional pollutants are below one pound per year, which is very low compared to most other manufacturing and service industries. The flow values are relatively low as well.

8.3 Toxic Weighting Factor Analysis

EPA's Office of Water uses toxic weighting factors (TWFs) to compare the relative toxicity of industrial effluent discharges. The toxic weighting factors applied to the photoprocessing industry are derived using the same methodology employed for other effluent guidelines, but are based on updated toxicity information. TWFs are used to calculate copper-based pound-equivalents, and are derived from EPA chronic aquatic life criteria (or toxic effect levels) and EPA human health Ambient Water Quality Criteria (or toxic effect levels) established for the consumption of fish. For carcinogenic substances, the human health risk level is set at 10^{-5}, (i.e., protective to a level allowing 1 in 100,000 excess cancer cases over background). Copper, a toxic metal pollutant commonly detected and removed from industrial effluent, is selected as the benchmark (i.e., the pollutant to which others are compared). EPA has used copper previously in TWF calculation for the cost-effectiveness analysis of effluent guidelines. While the water quality criterion for copper has been revised (to 12.0 μg/L), the TWF method uses the former criterion (5.6 μg/L) to facilitate comparisons with cost-effectiveness values calculated for other regulations.

The TWF for aquatic life effects and the TWF for human health effects are added for pollutants of concern. The calculation is performed by dividing the former copper criterion of 5.6 μg/L by the aquatic life and human health criteria (or toxic effect levels) for each pollutant, expressed as a concentration in micrograms per liter (μg/L):

$$TWF = \frac{5.6}{AQ} + \frac{5.6}{HHOO}$$

Where:

TWF = toxic weighting factor
AQ = Chronic aquatic life value (μg/L)
HHOO = Human health (ingesting organisms only) value (μg/L)

Toxic weighting factors for the 5 pollutants for which loadings are estimated and toxicity data are available are given in Table 8.3.

Table 8.3 Pollutant Toxic Weighting Factors

Pollutant	TWF
Ammonia	0.0022
Sulfate	5.6×10^{-6}
Silver	47
Iron	0.0056
Zinc	0.0051

Only one of the pollutants (silver) has a TWF greater than 1.0. This value is based on silver nitrate, however, which is not expected to exist in any appreciable concentration in photoprocessing effluent, as described in section 8.6.

8.4 Loads Associated with Photoprocessing Effluent

It is useful to estimate the total quantity of pollutants being discharged by the entire universe of facilities of a certain industrial category in order to compare the relative pollutant constituent releases within the industry, and also to compare these pollutant releases to those of other industries. The total pollutant loading for the amateur photoprocessing industry can be calculated from the flow and concentration values estimated in Chapter 6. Values for the other photoprocessing sectors can not be estimated due to lack of processing volume information. However, it is estimated that the amateur photoprocessing industry accounts for 44 percent of all photoprocessing, in correspondence to this segment's silver use as compared to all photographic silver use (data given in Table 4.3). The results presented in Table 6.8 show that the total 1994 amateur photoprocessing flow is estimated to be 2,250 million gallons per year, based on the additive process flow demands as reported in reference WEF 1994. The pollutant concentrations found in the total combined wastestreams, as presented in Table 6.3, are multiplied by this flow rate to calculate loads according to the following equation:

$$\text{Load (lbs/yr)} = \text{Mean Concentration (mg/L)} \times 2{,}250 \text{ million gallons} \times 3.785 \text{ L/gal} \times 2.205 \text{ lbs/kg} \times 1 \text{ kg}/10^6 \text{ mg}$$

Since the total unweighted load does not sufficiently describe the potential environmental impact of an industry's dicharge, toxic weighting factors as described above in Section 8.3 are used to calculate a toxic load, from the following equation:

$$\text{Toxic Load (lbs-eq/yr)} = \text{Load (lbs/yr)} \times \text{TWF}$$

Table 8.4 shows the estimated loads for each pollutant constituent, and the toxic loads for those pollutants which have a toxic weighting factor.

The table shows that the total expected annual load for the amateur sector this industry is 133 million pounds per year, and that approximately 9 million toxic pounds are discharged annually (99.9 percent of which are due to silver, for which the given toxic weighting factor is not representative). Once again, the amateur sector is estimated to account for 44 percent of all photoprocessing volume.

Table 8.4 Estimated 1994 Loads and Toxic Loads for the Amateur Sector of the Photoprocessing Industry

Pollutant Parameter	Concentration# Range (mg/L)	Concentration Average (mg/L)	Load (lbs/yr)	TWF	Toxic Load (lbs-eq/yr)
BOD	200-3,000	1,600	30×10^6	NA	
COD	400-5,000	2,700	51×10^6	NA	
TDS	300-3,000	1,650	31×10^6	NA	
TSS	<5-50	27	0.51×10^6	NA	
Ammonia	20-300	160	3.0×10^6	0.0022	6,610
TKN	30-350	190	3.6×10^6	NA	
Thiosulfate	100-1,000	550	10×10^6	NA	
Sulfates	50-250	150	2.8×10^6	5.6×10^{-6}	16
Silver	<0.1-5	10†	0.19×10^6	47*	8,830,000
Iron	<10-100	55	1.0×10^6	0.0056	5,784
Zinc	<0.75	0.75	14×10^3	0.0051	72
		Total =	133×10^6	**Total =**	8,842,482

Values from reference WEF 1994, pg. 10.

† The value range <0.1 - 5 is low compared to the concentration ranges presented in Table 7.3, for 95 percent silver recovery, combined wastestream (combined with wash water), of 5-20 mg/L. The value of 10 mg/L has been taken to be more realistic.

* This value is for the pure silver ion and does not accurately represent the actual toxicity of most silver compounds or complexes that would be expected to exist in photoprocessing wastewater.

As a comparison to the silver discharge value estimated above of 190,000 pounds (1994, amateur), the total silver loading before recovery can be calculated from the silver content of the film and paper used, the quantity processed, and the silver wash-out rates. The silver content of a variety of films and papers, and the proportions of these film and papers used by type for a typical photofinishing facility, are available in the literature. Assuming removal of all silver in color processing, and 80 percent silver removal in black-and-white processing, these values give the amount of silver rendered, in Troy ounces per 1000 square feet processed, to be 2.35 for paper, and 21.3 for film.(EPA 1991a, EPA 1991b) Multiplication by the total film and paper used for the U.S. amateur market allows the loadings calculation prior to silver recovery:

$$\begin{aligned} &\frac{2.35\ \text{Troy ounces}}{1000\ \text{ft}^2\ \text{paper}} \quad \text{x} \quad 4{,}115 \text{ x } 10^6\ \text{ft}^2\ \text{paper} && + \\ &\frac{21.3\ \text{Troy ounces}}{1000\ \text{ft}^2\ \text{film}} \quad \text{x} \quad 296 \text{ x } 10^6\ \text{ft}^2\ \text{film} && = \quad 16\ \text{million Troy ounce} \\ & && \text{or} \quad 1.1\ \text{million pounds silver} \end{aligned}$$

Thus, an overall recovery rate of 83 percent of this 1.1 million pounds would lead to the estimated 1994 amateur market discharge quantity of 190,000 pounds.

8.5 Qualitative Environmental Impact of Photoprocessing Effluent Constituents

This section examines the potential environmental impacts of some of the pollutants addressed earlier in this chapter as being characteristic of photoprocessing wastewater. Not all pollutants are listed due to lack of information. Examples of impacts include: impacts on human health, impacts on the health of aquatic organisms, impacts on operation of biological wastewater treatment systems, and aesthetics. Removal by typical activated sludge systems is also addressed.

Ammonia

Ammonia (NH_3) is one of the constituents of the nitrogen cycle. It is a concern because it can increase oxygen demand, promote eutrophication, and, when converted to nitrate, cause irritation of the gastrointestinal tract. The toxicity of ammonia to aquatic life is dependant on pH and dissolved oxygen level.(EPA 1981a) One study using a simulated photoprocessing waste stream showed an average removal of ammonia in activated sludge reactors of 53 percent.(Pavlostathis)

Cadmium

Cadmium is an extremely dangerous toxicant. In addition to being classified as a human carcinogen, cadmium could form organic compounds with mutagenic or teratogenic properties. In addition, conventional water treatment practices do little to remove cadmium, and it has been found to accumulate in the liver, kidneys, pancreas, and thyroid of humans and other animals. Cadmium also acts synergistically with other metals; its toxicity is considerably increased when combined with copper or zinc. Among aquatic organisms, fish eggs and larvae and crustaceans appear to be especially sensitive.(EPA 1981a)

Chromium

Chromium in industrial wastewaters exists primarily in hexavalent and trivalent states. Both are hazardous to man and aquatic life, but in photoprocessing wastewaters the trivalent form, which is considerably less toxic, predominates. Observed toxic effects on man include lung tumors, skin sensitization, corrosion of the intestinal tract, and inflammation of the kidneys. Lower forms of aquatic life are extremely sensitive to chromium. As with cadmium, chromium is not destroyed when sent to a POTW, and it either partitions to the biosolids or passes through the treatment stream. Removal by activated sludge systems is estimated to be 84 percent.(EPA 1981a, EPA 1982)

Cyanide

Cyanide is generally found in photoprocessing effluent in the form of ferri- and ferrocyanide (hexacyanoferrate) ions. These forms exhibit a low order of toxicity to most aquatic species, notable exceptions being crustaceans and algae. Hexacyanoferrate ions seem to cause no adverse effect on POTW biomass at typical levels, and treatment plant removal efficiency was reported at greater than 60 percent. As mentioned in Chapter 6, however, these ions release the cyanide ion when exposed to sunlight. Some of the cyanide ions will join with hydrogen ions to form hydrogen cyanide (HCN), depending on the pH of the solution. (The lower the pH, the greater the percentage of cyanide ions that will be present in the form of hydrogen cyanide). The cyanide ion is non-accumulative and comparatively non-toxic to humans. Toxicity to fish is dependent on pH, temperature, dissolved oxygen, and presence of other minerals in the water. It is generally more toxic to fish that it is to lower organisms.(EPA 1981a, EPA 1982)

Iron

Iron is an essential nutrient for all forms of growth, and does not have significant toxic impact on humans at any reasonable concentration. The presence of iron in water may encourage growth of iron oxidizing bacteria, resulting in formation of slimes that may affect aesthetic values of water bodies or block pipes. The recommended limit for iron in water supplies is based not on health concerns but on aesthetic and taste considerations.(EPA 1981a)

Lead

Lead is not easily excreted from the human body, and thus accumulates with repeated exposure over long periods of time. Possible effects include lead poisoning (plumbism) and cancer. Lead is also a concern among animals. More farm animals are poisoned by lead than by any other poison. Lead also causes suffocation of fish. Studies have shown POTW removal rates for lead of greater than 90 percent, although 80 percent is more common. Most of this is partitioned to the biosolids.(EPA 1981a, EPA 1982)

Silver

See Section 8.6.

Sulfates

Sulfates are not harmful in moderate concentrations (<1,000 mg/L). They occur naturally in waters, especially in the western United States. Thiosulfates are commonly found in photoprocessing wastewaters, as described in Chapter 6.(EPA 1981a). One study using simulated photoprocessing wastewaters found that about 35 percent of total COD of the composite photoprocessing wastewaters was thiosulfate and sulfite. COD reductions in the activated sludge reactors used varied between 84 and 96 percent, including the almost-complete removal of thiosulfate and sulfite (reduced to sulfate). Ammonia removal in the photoprocessing wastewater amended reactors, meanwhile, was lower than in the control reactor, possibly indicating inhibition of the highly-sensitive *Nitrobacter* species.(Pavlostathis)

Oxygen Demand (BOD & COD)

Certain levels of oxygen demand, depending on the receiving water body, will result in reduced Dissolved Oxygen (DO) levels. Aquatic organisms experience stress at reduced DO levels, both at the individual and population levels. Some fish species experience delayed hatching of eggs, interference with food digestion, decreased growth rate, decreased tolerance to other toxicants (including cyanide and lead), and reduced sustained swimming speed. These effects are usually more pronounced in livelier species (such as trout and salmon). BOD removal rates by activated sludge systems are generally around 90 percent.(EPA 1981a, EPA 1982)

Total Dissolved Solids (TDS)

Dissolved solids include carbonates, chlorides and other halides, sulfates, phosphates, nitrates, and trace substances. Although moderately high concentrations of TDS do not have serious health effects on humans, drinking water becomes unpalatable when TDS exceeds 2,000 mg/L. Tolerances of aquatic organisms for TDS is species specific, but although fish can slowly become acclimated to higher salinities, sudden exposures can often be fatal.(EPA 1981a)

Total Suspended Solids (TSS)

Suspended solids include organic (oil, tar, vegetable waste products) and inorganic (sand, silt) components. Impacts on aquatic ecosystems include reduced light penetration, which hampers photosynthetic activity, and clogging of gills and respiratory passages of organisms. POTW removal of TSS can be as high as 90 percent.(EPA 1981a, EPA 1982)

8.6 Toxicity and Speciation of Silver

Silver is present in a number of compound and complex forms in photoprocessing effluents. The concentrations, solubilities, and toxicities of these silver compounds are widely varied, and it is essential to have some understanding of their interrelation to better comprehend the possible adverse effect an effluent may have on the environment.

The most common silver complex found in photoprocessing effluent is silver thiosulfate, or $Ag(S_2O_3)_2$. This is a stable complex with a dissociation constant of 3.5 E-14, meaning that free silver ions (Ag^+) will not normally exist in any significant concentration. Silver nitrate ($AgNO_3$) is used extensively in the production of photosensitive films and papers, has the highest solubility of the silver salts, and is classified as a strong irritant to skin and tissue. Silver chlorate ($AgClO_3$) is moderately soluble, and is toxic when ingested. Silver chloride (AgCl) is soluble in solutions containing an excess of chloride ions, and in solutions of cyanide, thiosulfate, and ammonia, and is relatively toxic. Silver bromide (AgBr) and silver sulfide (Ag_2S) are insoluble silver compounds commonly found in precipitate form in photoprocessing effluents. Solubilities and Solubility Products (K_{sp}) of select silver compounds are shown in Table 8.5.

Table 8.5 Solubility and Solubility Product of Some Silver Compounds/Complexes

Silver Compound	Solubility (g/L H_20 at 25° C)	K_{sp}
chloride	$1.9 X 10^{-3}$	$1.8 X 10^{-10}$
chlorate	90	NA
bromide	$1.3 X 10^{-4}$	$3.3 X 10^{-13}$
nitrate	$2.16 X 10^{3}$	NA
sulfide (@20° C)	$1.4 X 10^{-4}$	$1.0 X 10^{-50}$

The free ionic form of silver combines rapidly with naturally-occurring substances to form less toxic substances. For example, silver chloride complexes are three hundred times less toxic and silver sulfide complexes are one million times less toxic than free silver.(Dufficy) Table 8.6 demonstrates this relative toxicity for fathead minnows.

Table 8.6 Percent Mortality of Fathead Minnows Acutely Exposed to Concentrations of Different Silver Compounds

Silver Compound	Mean measured total silver concentration, mg/L	Mean free silver ion concentration, mg/L	Percent Mortality			
			24 h	48 h	72 h	96 h
Silver Nitrate	0.065	0.065	100	100	100	100
	0.029	0.029	80	100	100	100
	0.013	0.013	5	5	5	10
	0.0058	0.0058	5	5	5	5
Silver thiosulfate complex [a]	280	0.12 X 10^{-6}	5	5	5	10
	140	0.33 X 10^{-6}	0	0	0	0
	70	0.80 X 10^{-6}	0	0	0	0
Silver sulfide dispersion [b]	240	$<10^{-11}$	0	0	0	0
	37	$<10^{-11}$	0	0	0	0
Silver chloride (2000 ppm Cl) [a]	4.6	1.03 X 10^{-4}	40	40	40	40
	2.0	1.01 X 10^{-4}	5	10	10	10
	0.38	1.01 X 10^{-4}	0	0	0	0

Source: Dufficy
a. Calculated from the mean measured free silver ion activity
b. Calculated from the relationship $[Ag^+]^2[S^2]=K_{sp} = 10^{-50}$

The free silver ion is an effective bactericide, and thus it can interfere with biological treatment systems. However, one study indicated that silver thiosulfate concentrations of 100 mg/L caused no negative impact on unacclimated activated sludge. The study also states that photoprocessing effluent with a silver concentration as high as 10 mg/L could be handled by a biological treatment system, and that the expected effluent from the treatment system would be less than 20 ug/l of soluble silver, even without dilution from other treatment plant inputs. Meanwhile, silver nitrate and silver chloride at concentrations of 10 mg/L were found to cause inhibition between 43 and 84 percent.(Bard)

Silver that settles is removed from the treatment plant in the form of biosolids. There is currently no EPA biosolids criteria for silver. POTW biosolids are often disposed by landspreading or landfilling. Laboratory tests on biosolids containing silver in concentrations from 19 to 83,000 mg/kg showed no release of silver to the elutriate. Field tests indicated that silver was effectively bound up by the soil.

No evidence could be found linking photoprocessing effluent to adverse human health effects. However, silver compounds can be absorbed into the circulatory system and reduced silver deposited in various tissues of the body, possibly resulting in a permanent greying of the skin and mucous membranes known as argyria. Also, concentrations from 0.4 - 1 mg/L have been shown to cause kidney, liver, and spleen damage in rats.(EPA 1981a) Some local authorities in the United States consider silver to be a hazardous waste in concentrations greater that 5 mg/L, which is far less than some of the untreated effluent silver concentrations as documented in Chapter 6.(EPA 1991a) As mentioned in Section 8.3, several other constituents in photoprocessing effluent can also have carcinogenic and systemic health effects on humans.

LC_{50} concentrations of silver for a number of common aquatic organisms varies between 0.004 mg Ag/L and 0.2 mg Ag/L.(Bard) Other silver salts, such as silver chloride and silver nitrate, are also considerably toxic to fish. One study claims that "anthropogenic inputs of silver from the Point Loma discharge off San Diego, CA can account for essentially all of the silver in coastal waters along the United States-Mexico border during summer conditions", and that "silver is one of the most toxic elements for marine invertebrates."(Sanudo)

The silver thiosulfate complex, however, is considerably less toxic; the 96 hour LC_{50} was found to be greater than 250 mg Ag/L. Other work indicated that a model laboratory ecosystem including rotifers, *Daphnia*, algae, mussels, and fish remained viable during the ten week study period in spite of continuous exposure to silver thiosulfate at concentrations as high as 5 mg Ag/L.(Bard) Despite this, it is still desirable to remove as much silver thiosulfate from the wastestream as possible, since thiosulfate accounts for a major portion of the oxygen demand in photoprocessing effluent.(Hendrickson)

Bioaccumulation of silver in clams in the vicinity of the Palo Alto Regional Water Quality Control Plant (RWQCP) has been well documented. Silver concentrations in clams near the RWQCP discharge channel were found to be from 6 to 55 times the levels of silver found in clams in other areas of the San Francisco Bay. After initiating a silver reduction pilot program, silver concentrations in the clams showed a continual decline. However it is not clear if the original higher concentrations of silver caused any negative impacts on the clams.(WEF 1994)

References

Bard: Bard, C.C., et al, "Silver in Photoprocessing Effluents." Journal of the Water Pollution Control Federation, Vol. 48, 1976. pp 389-394.

Calif. DHSa: California Department of Health Services, Alternative Technology Section, Toxic Substances Control Division, "Waste Audit Study: Photoprocessing Industry," 1989.

Calif. DHSb: California Department of Health Services, Alternative Technology Section, Toxic Substances Control Division, "Reducing California's Metal-Bearing Waste Streams," 1989.

Cook: Cook, M.M. and Lander, J.A., "Use of sodium borohydride to control heavy metal discharge in the photographic industry." Journal of Applied Photographic Engineering, Vol. 5, No. 3, 1979. pp 144-147.

Dufficy: Dufficy, T.J. et al, "Silver Discharge Regulations Questioned." Water Environment & Technology, April 1993. p.54.

EPA 1976: USEPA, Office of Water, Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Photographic Processing Subcategory of the Photographic Point Source Category, EPA 440/1-76/0601, July 1976.

EPA 1980: USEPA, Office of Water, Ambient Water Quality Criteria for Silver, EPA 440/5-80-071, 1980.

EPA 1981a: USEPA, Office of Water, Guidance Document for the Control of Water Pollution in the: Photographic Processing Industry, EPA 440/1-81/082-9, April 1981.

EPA 1981b: June 15, 1981 Affidavit of Echardt C. Beck, Assistant Administrator, EPA, submitted under Natural Resources Defense Council et. al. Versus EPA, 12 ERC 1833 (March 9, 1979)

EPA 1982: USEPA, Office of Water, Fate of Priority Pollutants in Publicly Owned Treatment Works, EPA 440/1-82/303, September 1982. p 61.

EPA 1987: USEPA, Office of Water Enforcement and Permits, Guidance Manual on the Development and Implementation of Local Discharge Limitations Under the Pretreatment Program, December 1987.

EPA 1991a: USEPA, Office of Research and Development, Guides to Pollution Prevention: The Photoprocessing Industry, EPA/625/7-91/012, October 1991.

EPA 1991b: USEPA, Office of Research and Development, Waste Minimization Opportunity Assessment: A Photofinishing Facility, EPA/600/2-91/039, August 1991

EPA 1994: USEPA Office of Policy, Planning, and Evaluation, Sustainable Industry: Promoting Strategic Environmental Protection in the Industrial Sector - Photoimaging Industry, Phase 1 Report, June 1994.

Hendrickson: Hendrickson, T.N. and Dagon, T.J.; U.S. Patent 3,594,157; July 20,1971; assigned to Eastman Kodak Company.

Lewis: Lewis, R.J. Sr.[Ed.], Condensed Chemical Dictionary, Twelfth Edition, Van Nostrand Reinhold Company, 1994.

Kirk: Kirk-Othmer [Eds.], Encyclopedia of Chemical Technology, Volume 21, 1983. pp 16-23.

Kodak 1980: Eastman Kodak Company, "Recovering Silver from Photographic Materials," Publication J-10, 1980.

Kodak 1989a: Eastman Kodak Company, "Choices - Choosing the Right Chemicals for Photofinishing Labs," Publication J-35, 1989.

Kodak 1989b: Eastman Kodak Company, "Disposing of Mini-Lab Effluent," Publication J-20, 1989.

Kodak 1990: Eastman Kodak Company, "Disposal and Treatment of Photographic Effluent. In Support of Clean Water." Publication J-55, 1990.

Pavlostathis: Pavlostathis, S.G. and Jugee, S., "Biological Treatment of Photoprocessing Wastewaters." Water Science and Technology, Vol. 29, No. 9, 1994. pp 89-98.

PMA 1995: Marketing Research Department, The 1994-95 PMA Industry Trends Report, Photo Marketing Association International (PMA), Nov. 1995.

Sanudo: Sanudo-Wilhelmy, S.A., and Flegal, A.R., "Anthropogenic Silver in the Southern California Blight: A New Tracer of Sewage in Coastal Waters." Environmental Science Technology, Vol.26, No. 11, 1992. pp 2147-2150

Silver CMP: Silver Council and Association of Metropolitan Sewerage Agencies, "Code of Management Practice for Silver Dischargers," November 1996.

Sribnick: Sribnick, L., "The Color Darkroom - How to tell when your color chemicals and printing papers go bad, and how to make them last longer." Popular Photography, April 1986. p.18.

WEF 1994: Water Environment Federation, Pollution Prevention Committee, Controlling Silver Discharges in Wastewater: Technical Guidance Manual for Silver Discharges, 1994.

WSS 1993: The Silver Institute, World Silver Survey 1993, 1993.

WSS 1996: The Silver Institute, World Silver Survey 1996, 1996.

Appendix A. Calculation of Total United States Surface Area of Photographic Film and Paper Developed for Amateur Market

<u>Values from Literature</u>*		Surface Area per 24 <u>Exposure Role (ft^2)</u>
Rolls Processed 1994: 715.5 million	→ 659 million rolls 35mm	0.440
	→ 48.7 million rolls 110/126	0.131
	→ 5.01 million rolls disc	Not Available
	→ 2.86 million rolls other	Not Available

Exposures Processed 1994: 17.58 billion → 16.65 billion color print
→ 615 million slide
→ 316 million black-and-white

Original Print Market Share:
- Single Prints 53.4% versus Twin Prints 46.6%
- 3 ½ x 5 inch 59.4% versus 4 x 6 inch 40.6%

<u>Assumptions and Simplifications</u>

- Assume all rolls of 24 exposure, supported by result:
  17.58 billion exposures/715.5 million rolls = 24.6 exposures/roll

- Based on information that photoprocessors gain 75% of revenue from original prints and 14% from reprints and enlargements, assume that paper surface area of reprints and enlargements is 14/75 or 18.6 % of original print area.

- Include back-and-white photoprocessing in with color, because while greatly simplifying the calculation the only waste steam affected in these calculations is bleach, effected by less than 2 percent.

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* All values taken from reference PMA 1995, except surface area per roll values from reference EPA 1991a.

Calculation of Film Surface Area

35mm: 659 million rolls 35mm x 0.440 ft^2/roll 24 exposures = 290 million ft^2
110/126: 48.7 million rolls 110/126 x 0.131 ft^2/roll 24 exposures = 6.37 million ft^2
Total: 296 million ft^2
Note: Total does not include disc and "other" film area due to lack of surface area/roll data.

Calculation of Print Paper Surface Area

59.4% 3 ½ x 5: (16.65 billion + 316 million) x 3.5" x 5" x 1 ft^2/144 in^2 x .594 = 1.22 billion ft^2
40.6% 4 x 6: (16.65 billion + 316 million) x 4" x 6" x 1 ft^2/144 in^2 x .406 = 1.15 billion ft^2
Total: 2.37 billion ft^2

Total with twin prints (46.6% of exposures): 2.37 billion ft^2 x 1.466 = 3.47 billion ft^2

Total with reprints and enlargements (18.6% of original prints):
3.47 billion ft^2 x 1.186 = 4.12 billion ft^2