Chapter 1

HAZARDOUS WASTE GENERATION AND DISPOSAL PRACTICES OF BERKELEY PHOTOFINISHING LABORATORIES

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The Bay Area produces 12.3 million tons of hazardous waste annually. Small generators, those who produce less than 1,000 kilograms of waste per month, are responsible for one to ten percent of this waste and comprise 90 percent of total waste generators (Jackson, 1983, pers. comm.). Under federal law, small generator disposal practices are not regulated. State regulations do exist, but a lack of manpower prevents enforcement. Meanwhile, hazardous wastes end up in backyards, landfills, sewage streams and vacant property, endangering human health and the environment.

Little information exists on the quantities, types and disposal of waste produced by small generators. Many small generators know little or nothing about the nature of their wastes, proper disposal methods and current regulations which apply to them. The high costs sometimes involved in the proper handling of hazardous waste may be prohibitive to a small generator with only a small waste stream.

I propose to survey small photographic labs in Berkeley to assess types, quantities and disposal methods for wastes produced. With this information I hope to assess how dangerous current disposal methods are to the environment and propose alternative methods for dealing with wastes.

Past Work

A report by TRW (TRW, 1979) represents the most extensive study available on small generators of hazardous waste, including photoprocessing laboratories. The report contains information gathered from surveyed businesses and other sources on photoprocessing waste characterization, treatment, and storage and disposal practices. No information is given about specific chemical compositions, amounts and hazards of the wastes.

A study by SCS Engineers (SCS Engineers, 1982) compiles results from surveyed businesses to determine sources of pollution to the San Fernando Valley basin groundwater. No breakdown is given of the chemical compositions or concentrations of the photoprocessing wastes found from the surveys, severely limiting the usefulness of the data. The report rates photographic chemicals as having low to moderate toxicity, although it indicates that some organic photoprocessing chemicals are not only toxic, but can also react with other chemicals to form toxic and carcinogenic chemicals. Again, no information is given about what and how common these other chemicals and reactions are.

The Department of Health Services (DOHS) Handbook of Industrial Waste Composition in California - 1978 (Storm, 1982) lists waste data compiled from 1978 state hazardous waste manifests. Any time a generator contracts with a hazardous waste hauler to have wastes taken to a licensed dumpsite, he or she must provide the hauler and DOHS with a document (manifest form) which details the amount of waste, its chemical and mineral composition, and its maximum and minimum percentage solution. The DOHS data are useful because they provide a more specific breakdown of chemical compositions than most other publications.

The usefulness of the DOHS report for my purposes is limited by three factors: (1) typical load sizes range from 1,600 to 5,000 gallons, indicating that in general only large processing operations dispose of wastes in licensed waste dumps; (2) no information is given on rates of chemical waste production; (3) the chemical compositions listed fail to reflect reactions between combined waste streams.

Artist Beware (McCann, 1979), an excellent book on the hazards of working with art and craft materials, provides an extensive inventory of photographic chemicals and the hazards they pose to the photofinishing lab worker. The book does not address wastes.

Overview of Photoprocessing: Processes and Chemicals

Photoprocessing laboratories are involved in processing two types of film: color and black and white. Many of the same chemicals are used in both color and black and white film processing. Black and white photoprocessing chemicals vary little from formula to formula, and product compositions are easily obtained. Color photoprocessing is more complicated, and chemical compositions of formulas are often protected as trade secrets. However, Material Safety Data Sheets, which must list all hazardous components of a commercially sold solution, are easily obtained by calling most photoprocessing chemical manufacturers.

Black and white - Black and white film consists of an emulsion of silver halides (AgI, AgCl, AgBr) suspended in gelatin. When exposed to light, these halides undergo chemical reactions to form invisible latent images which are later made visible by development (Eaton, 1957).

The first step in black and white film processing involves use of developers which change the light-exposed grains of silver halide to metallic silver. Commonly used developers are hydroquinone and monomethylpara-aminophenol sulfate. Developers are usually alkaline solutions which are skin and eye irritants and toxic by inhalation and ingestion (McCann, 1979).

Preservatives extend the useful life of developing baths by preventing oxygen from reacting with the developer to form colored oxidation products (Eaton, 1957). Sodium sulfite, a common preservative, is itself moderately toxic by inhalation or ingestion, but decomposes to produce sulfur dioxide gas which can cause chronic lung problems in laboratory workers (McCann, 1979).

When the film has reached the desired stage of development, it is placed in a stop bath to halt the silver halide-to-silver reaction. All stop baths contain acid, usually acetic acid 28% or glacial acetic acid, to neutralize (and thereby halt) the alkaline developing agents. Acetic acid, in concentrated solutions, is highly toxic by inhalation or ingestion. In the highly diluted form used, it can cause chronic bronchitis from constant inhalation (McCann, 1979). The stop bath gradually loses its acidity because of contact with alkaline developers. Periodically the bath is replenished by addition of 28% acetic acid. Eventually, the bath must be disposed of, due to build-up of unwanted by-products of development (Eaton, 1957).

Following the stop bath, developed film is placed in a fixing bath which removes the unexposed silver halides by forming stable complex compounds with the silver ions (Eaton, 1957). Ammonium and sodium thiosulfate, also referred to as "hypo," are common fixing bath ingredients. Thiosulfate can decompose to sulfur dioxide gas (McCann, 1979).

Other common components of fixing baths are acids (sulfuric) or acid salts (sodium bisulfate). Fixing bath pH generally ranges from about 3.0 to 5.2. When pH or silver content exceeds the manufacturer's specified limit, the fixing bath is considered exhausted and must be recycled or disposed of. Spent fixer can be treated to recover metallic silver. Such treated fixer can sometimes be recycled for further use (Eaton, 1957).

The process just described produces a negative image from which positive prints can be made. Another process, called reversal processing, develops a positive image by the addition of a bleaching step after the developing agent. The bleach bath removes the developed metallic silver (negative image), and the remaining silver halides are exposed to light and redeveloped to produce a positive image. Potassium dichromate and sulfuric acid are commonly used in black and white film bleaches and are converted to silver sulfate and chromic sulfate in the process (Eaton, 1957). Potassium dichromate is a suspected carcinogen, and sulfuric acid is reactive, corrosive, toxic and can release sulfur oxide gases (McCann, 1979).

Other black and white processes involve toners, intensifiers and reducers. Toning replaces silver with another metal, such as gold, selenium, uranium, platinum or iron. Other chemicals involved are sodium and potassium sulfide, which can release toxic hydrogen sulfide gas when combined with acid. Selenium salts combined with acid form toxic hydrogen selenide gas. Thiourea, a chemical found in some toners, is a suspected carcinogen (McCann, 1979).

Intensification usually involves addition of heavy metals to the silver. Some chemicals involved are mercuric chloride with ammonia or sodium sulfite, mercuric salt bleach followed by a silver nitrate/potassium cyanide solution, hydrochloric acid and others. Potassium and sodium cyanide are highly toxic by ingestion, and addition of acid leads to formation of highly poisonous hydrogen cyanide gas (McCann, 1979). Mercury is highly toxic. Reduction usually involves potassium ferricyanide, which can also release hydrogen cyanide gas when heated (McCann, 1979).

Color - Color negative processing involves a dye coupling developer which simultaneously develops a color and a silver image. Color transparency processing involves development with a black and white developer, re-exposure to light and development with a dye coupling developer. Bleaching to remove silver images, fixing, and hardening and stabilization of the dye image follow (McCann, 1979).

Color developers contain similar chemicals to black and white developers plus color coupling agents and solvents including benzyl alcohol, ethylene glycol, amines and other chemicals. Color couplers are often highly toxic by ingestion, inhalation and skin contact (McCann, 1979).

Sulfamic acid, a bleach, is toxic and releases sulfur dioxide when heated or additional acid is added. Formaldehyde and succinaldehyde, used in hardeners, are both toxic. Hydroxylamine sulfate, a neutralizing solution, is a suspected teratogen (McCann, 1979).

Methods

The purpose of this study is to determine the types, amounts and potential for harm of chemicals disposed of by Berkeley photoprocessing labs. It should be noted that photoprocessing laboratories are just one of several industrial groups producing photofinishing wastes. Photographic studios, portrait studios, arts and graphics businesses, motion picture producers, and professional printers and publishers all process film and thus produce photofinishing wastes. This study focuses exclusively on photoprocessing laboratories, where film processing is the primary activity.

To determine types and amounts of waste produced, a survey was administered to owners and managers of photoprocessing labs. Businesses to be surveyed were selected from the Oakland phone book yellow pages. A list of 24 labs thought to be engaged primarily in photofinishing and located in Berkeley was compiled. All 24 businesses were contacted. Three were no longer in business, and nine were retail outlets which were not engaged in film processing. Out of the remaining twelve, four were interviewed. I discovered that two of the 24 labs are actually located in Oakland or other neighboring areas of Berkeley. These labs were included in the survey.

The survey form used to interview businesses was developed at the Association of Bay Area Governments with input from myself and other class members (see Appendix to Section IV.B.). Questions asked fall into four categories: types, amounts and disposal methods for wastes generated; information about size and production of the business; familiarity with regulations; and willingness to use alternative methods of disposal, such as recycling and waste exchange.

All businesses were initially contacted by phone, at which time I explained the purpose of the study and arranged an appointment with the four businesses which agreed to be interviewed.

The survey was administered face to face in an interview format at the site of operation, permitting first-hand observation of chemical handling procedures and safety.

Data

Four photoprocessing labs agreed to be surveyed. Two are engaged in exclusively black and white processing, and two in exclusively color processing. Of the color labs, one is too large to be considered a small generator of waste.

Background data on size of operation is given in Table 1. Size of production varied a great deal, from less than 300 roles of film processed per year to over 500,000. Number of employees ranged from 4 to 50.

Business	Type of Film Processed	# Employees	Land Area in Square Feet	# Years in Operation	# Roles of Film Processed/Year
1	black/white	*	not known	not known	7300
2	black/white	4	900	12	less than 3000
3	color	38	3000	18	73,000
4	color	50	25,000	25	500,000

*used primarily by UC Berkeley students for processing film for class assignments

Table 1. Vital Statistics of Surveyed Businesses

Table 2 lists by process the types and amounts of chemicals used and disposed of. Both color labs used Kodak C-41 photoprocessing chemicals. The large color lab used Kodak EP-2 as well. The black and white labs primarily used Kodak Dektol, Kodak D-76 and Ilford Ilfospeed 2000 developers, acetic acid stop baths and Kodak rapid fix fixer. With the exception of the large color lab, the amount of waste chemical disposed of is small, ranging from 14 to 350 gallons per month.

In all cases chemical disposal is to the sewer. Contaminated containers are thrown into the municipal garbage. Rinsing takes place occasionally to recover the maximum amount of chemical for use.

June through September are peak months of production, except in one lab, primarily used by students, where these months are a lull. The summer peak corresponds to the Bay Area's lowest season of rainfall and therefore least burden on sewage treatment plants, but also least dilution of sewage.

A question regarding emergency plans for spills, leaks or accidents drew a variety of responses. Two businesses report having eyewashes and emergency numbers for Kodak and Ilford, the two largest

Business	Brandname: Manufacturer	Hazardous Ingredients	Concentration*	Undiluted Amt. Disposed**	Diluted Amt. Disposed**
Developers					
1	Kodak: Dektol	Hydroquinone P-methylaminophenol sulfate	65-70% 30-35%	20 gal./mo.	140 gal./mo.
	Kodak: D-76	Hydroquinone P-methylaminophenol sulfate	b	20 gal./mo.	140 gal./mo.
2	Kodak: Dektol	a	a	36 oz./mo.	2 gal./mo.
	Kodak: D-76	a	a	4lb./mo.	4-6 gal./mo.
	Kodak: DK50	Sodium metaborate	b	0.34 oz./mo.	8 oz./mo.
	Kodak: HC 110	Hydroquinone 2,2'-Iminodiethanol 2-Aminoethanol	5-10% 50-55% 5-10%	16 oz./mo.	2 gal./mo.
	Ilford: Ilfospeed 2000	b	b	5 gal./mo.	24 gal./mo.
3	Kodak: C-41	Potassium carbonate Potassium hydroxide	31-35% 1-5%	c	100 gal./mo.
4***	Kodak: C-41	a	a	150 gal./wk.	240 gal./wk.
	Kodak: EP-2	b	b	c	510 gal./wk.
Stop Baths					
1	Kodak	Acetic acid	b	2 oz./mo.	1 gal./mo.
2	Misc.	Acetic acid	b	1 oz./mo.	½ gal./mo.
3	Kodak	Acetic acid	b	c	c
4	Kodak	Acetic acid	b	c	c
Fixers					
1	Kodak: Rapid fix	Sulfuric acid	7-12%	24 gal./mo.	120-240 gal/mo
2	Kodak: Rapid fix	a	a	3 gal./mo.	15 gal./mo.
3	Kodak: C-41 fix	Ammonium sulfate Sodium bisulfate	50-55% 5-10%	c	50 gal./wk.
4	Kodak: C-41 fix	a	a	c	113 gal./wk.
	Kodak: EP-2 bleach/fix	b	b	c	85 gal./wk.
Bleaches					
3	Kodak: C-41 bleach	Ammonium bromide Acetic acid Potassium nitrate	25-30% 10-15% 5-10%	c	50 gal./wk.
	Kodak: paper process bleach, part A & B	A: Ammonium thiosulfate Sodium bisulfate	45-50% 5-10%	c	c
		B: Ammonium (ethylenedinitrilo tetraaceto) ferrate Ethylenediaminetraacetic acid	35-45% 5-10%	c	c
4	Kodak: C-41	a	a	c	113 gal./mo.

Legend: a information listed above-same table; b information unavailable at time of writing; c respondent did not know; * from label or material safety data sheet; ** survey, this report; *** large color lab

Table 2. Hazardous Chemicals Disposed of in Berkeley Photoprocessing Labs.

photoprocessing chemical manufacturers. One company keeps chemicals in a room with sealants around the wall/floor joints to contain chemicals in the event of a spill, whereas another thought the chemicals used in photoprocessing are not dangerous enough to warrant any special plans. The large color lab has an elaborate system for dealing with spilled or contaminated chemicals. The chemical is collected in a 200-gallon tank and metered slowly into the sewer system.

Two of the labs interviewed report some familiarity with federal and state hazardous waste regulations, whereas two report no familiarity. None of the labs report having ever applied for a DOHS hazardous waste permit, and only the large color lab has effluent testing and a waste water discharge permit from the East Bay Municipal Utilities District (EBMUD).

All of the companies recycle their spent fixer for silver. Three own silver recovery equipment, which in all cases produces a profit, and one sells a silver/fixer sludge to a recycling company. Both color labs recycle Kodak C-41 bleach, but do not know what by-products are produced or disposed of.

Only one lab owner feels that the alternative waste disposal methods listed on the survey apply to photoprocessing labs. She indicates she would use a permanent collection site, a community dump day, and a hazardous waste exchange if available, and might use a recycling service or collection service. She is willing to pay less than $25/month for these services. The rest of the labs feel that sewer disposal is adequate and not harmful environmentally.

Discussion

Environmental hazards of waste - With the exception of the large color lab, the amount of waste produced in Berkeley labs is small. Photoprocessing labs use copious amounts of water during processing, and mixed photo solutions are generally quite dilute. The main hazards connected with waste chemicals found in the survey are abnormal pH and high biological oxygen demand (BOD).

Stop baths and fixers both have an acid pH. By the time of disposal, however, the pH of both has usually been raised to an acceptable level by contact with developer solutions. Developer solutions are alkaline, but rarely exceed pH 10. Often they are disposed of simultaneously with acids, somewhat neutralizing the effluent (Deegan, 1984, pers. comm.).

Sewer disposal of small amounts of most commonly used photoprocessing chemicals should pose no threat to the environment when sewage treatment facilities include bio-activation, secondary aeration and clarifiers (Deegan, 1984, pers. comm.). EBMUD's sewage treatment fulfills these requirements. Use of heavy metals (other than silver) in photoprocessing is not found in any of the businesses surveyed.

Recycling - Silver is considered a priority pollutant, since in some forms it is highly toxic to micro-organisms (Deegan, 1984, pers. comm.). All labs surveyed recover silver, and with the price of silver high enough to assure a profit, I suspect that most labs do.

Many inexpensive and simple recycling processes are available for extending the useful life of photoprocessing chemicals. Such processes save money for labs and result in less effluent. When film is taken from one solution to the next, it carries a layer of the previous solution into the new bath. Build-up of carry-over products reduces the effectiveness of the photoprocessing solutions and leads to premature disposal. Squeegees (Figure 1) can reduce carry-over by more than 75% (Eastman Kodak, 1982).

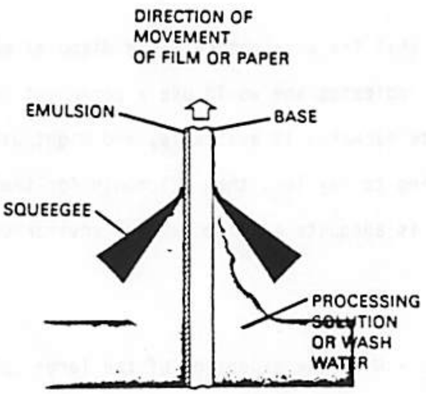

Figure 1. Squeegee.
Source: Eastman Kodak Co., 1982.

When exposed to air, photoprocessing chemicals oxidize, evaporate, absorb carbon dioxide and are contaminated with dust and dirt. The use of floating lids over chemical storage containers can more than double the solution's useful life (Eastman Kodak, 1982).

Ferricyanide bleaches can be regenerated by the addition of ferrous sulfate to precipitate complex cyanide. This technique results in the generation of a Prussian Blue ferri-ferrocyanide sludge. Ozonation and persulfate addition as bleach treatments produce no sludges (TRW, 1979).

Worker safety - As noted earlier in the "Overview of Photoprocessing" section of this report, many photoprocessing chemicals are toxic by inhalation, ingestion or skin contact, and some can release toxic or irritating gases. Most labs I contacted about interviewing responded with comments such as, "We don't use any poisons here," or "Nothing we use here could hurt anyone." Such comments demonstrate a general lack of awareness about occupational hazards of photoprocessing.

During two of the interviews, I observed inadequate ventilation of darkrooms and workers without proper safety equipment such as gloves. One lab owner commented that they had discovered that a certain chemical was an excellent floor cleaner after accidentally spilling it. They routinely use it to clean the floors now! Although much work has already been done on worker safety, increased education of management and workers is needed.

Conclusion

Small generation of photoprocessing wastes appears not to pose a great hazard to the Bay Area environment. Sewage treatment facilities are adequate to treat the effluent. Even so, no small generator should dump large amounts of acid or alkaline substances down the drain separately, no heavy metals should ever be disposed of into the sewer, and containers should always be thoroughly rinsed prior to disposal. Where economical, recycling measures should be instituted within individual labs. But, because most recycling processes now available are designed for use within the lab, and effluents are extremely dilute, a community recycling center would not be economical or of use to photofinishing labs. Most importantly, workers should familiarize themselves with the hazards associated with the chemicals they work with and take the proper precautions.

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