Chapter 2

HAZARDOUS MATERIALS AND WASTES FROM BERKELEY'S PRINTERS

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The problem caused by generation of hazardous wastes in large quantities is well known and well publicized. Small quantity generation, however, is an often overlooked facet of the hazardous waste problem. Small generators such as laboratories, small businesses, and households need to be regulated at the community level. Before appropriate steps can be taken for the management of the small generation problem, an assessment must be made of its nature and quantity. How big is the problem? What are the areas of concern? Data are needed so that we can determine if small generators of hazardous wastes are a problem, and if so, which ones.

This report analyzes the hazardous materials used and disposed of by one type of small generator, the printers of Berkeley. A quantitative assessment of the problem is made by surveying various businesses. It is hoped that this report will be a useful tool in developing a community management plan for Berkeley's small generators of hazardous waste.

Previous Work

Two previous studies of the production of hazardous wastes by printers have concluded that there are some potential pollution problems. The Conference on Environmental Aspects of Chemical Use in Printing Operations (EPA, 1976) covers all types of printing and reviews some of the occupational and environmental hazards. The conference finds that hydrocarbon emissions from solvents pose an air pollution problem, and that many of the chemicals in use pose toxicological hazards to exposed workers. The TRW Report (TRW, 1979) surveys small businesses, including printers, to examine the general types of waste produced. The report concludes that there is a potential waste problem from some of the solvents, inks, and dyes used in printing operations, and that further study is needed.

This report deals with the hazardous materials used by printers in Berkeley, the hazardous wastes generated, and the resulting occupational ane environmental problems.

Methodology

Businesses with Berkeley addresses were selected from the phone book under the heading "printers". Photocopiers and graphics shops were ruled out and a total of 25 printers in the Berkeley area were contacted. Of these, 11 cooperated and 2 were too large for the purposes of this survey, giving a total of 9 usable surveys. Each printer completed a standardized survey form (see Appendix to Section IV.B.), and additional information was gained from interviews with print shop managers. Where information was vague, deleted, or inconclusive, best estimates are made by cross-referencing other surveys and previous works. The report focuses on offset lithography, since that is the process employed by most Berkeley printers, but also touches on letterpress, gravure, and flexography.

Results

Surprisingly, the printers in Berkeley generate very little in the way of hazardous wastes. The results of the survey show the printers to be small producers, and they use very small quantities of ink, solvents, and photochemicals. The chemicals either stay with the product, evaporate, or are recycled.

Income of Berkeley printers ranges from $5,000 to $15,000 per month and production ranges from 1,500 to 3,500 pounds per month. Of the printers surveyed, 9 employ offset as their major process, 2 letterpress, 1 gravure, and none flexographic.

An average of about 20-30 pints of ink are used per shop per month (Table 1). Excess ink is

Substance	Average/Shop	Estimated Berkeley Total
solvents	6 gal/mo.	144 gal/mo.
plate developer	1 gal/mo.	24 gal/mo.
film developer	3 gal/mo.	72 gal/mo.
other photochemicals i.e., fixers stopbaths	4 gal/mo.	96 gal/mo.
ink	20-30 pts/mo.	480-720 pts/mo.

Table 1. Hazardous Materials Used. Estimated Berkeley Totals Are Based on 24 Shops.

wiped off with rags which are then recycled. Rag usage averages about 250 rags per shop per month.

Cleaning solvent usage averages about 6 gallons per shop per month. Most evaporates and the small amount of waste is recycled with the rags. One place did report dumping solvents into its septic tank (Table 2). About 1 pint of rubber rejuvenator is used per shop per month.

Adding the cleaning solvent to the solvent content of ink (about 15%) gives an average of about 8 gallons of solvent evaporated from each shop per month.

Photochemicals, such as developers, fixers, hardeners, and stop baths are usually recycled, as is film. Smaller users, those using under 3 gallons per month, flushed liquid waste into septic

METHOD OF WASTE DISPOSAL

Substance	Sewer	Septic	Recycle
solvents	--	1 gal/mo.	--
photochemicals	2 gal/mo.	10 gal/mo.	6 gal/mo.

Table 2. Method of Waste Disposal, Average Per Shop Per Month.

tank or sewer. The composition of this waste stream could not be estimated, but the total volume averages about 2-3 gallons per shop per month.

Discussion

Some background information on printing is useful to better understand the chemicals employed and the exposure routes to worker and environment. Printing is the process of transferring an image to a substrate (Gikis et al., 1983). The medium or coloring agent is ink and is composed of a vehicle to give fluidity and a pigment which forms the image. Substrates or surfaces can be wood, glass, metal, paper, cardboard, or film.

There are four major printing processes: letterpress, gravure, flexographic, and lithographic offset. Letterpress consists of transferring a thin film of ink from the raised printing surface of the typeform to the paper by pressing the two together. Flexographic printing is essentially roll-fed letterpress except the typeplate is made of flexible rubber, and the ink is more fluid, because it has greater solvent content (Gikis et al., 1983). The gravure process transfers very fluid ink from the cells of an etched cylinder to the paper, which can be sheet-fed or roller (web) fed.

Sheet-fed offset lithography is the most common printing process used in Berkeley. The ink is transferred from a typeplate roller to a rubber blanket roller, and then to the paper. A photographic plate, usually aluminum, is prepared so that its image areas absorb ink and repel water, whereas the non-image areas repel ink and absorb water. The prepared plate is wrapped around the plate roller, which is first wet by water, and then by ink (Figure 1) (EPA, 1976). Lithographic inks are generally lower in solvent content (Gikis et al., 1983).

Hazardous Materials

Hazardous materials are defined as being toxic, carcinogenic, flammable, or corrosive. A variety of the photochemicals are corrosive and caustic, and most of the solvents used are flammable.

Some of the ink components and solvents are either carcinogenic or toxic.

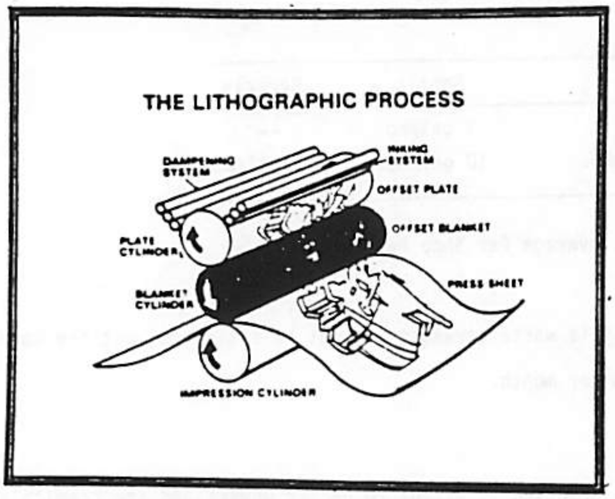

Figure 1. The Lithographic Process.
Source: EPA, 1976.

Kodak Developer A and B is the most common type of developer used to process film for print making. It contains hydroquinone, potassium hydroxide, potassium bromide, and potassium metasulfate. Hazards are related to the potassium hydroxide which has a pH of 12.5 and is caustic (White, 1973), and potassium bromide, which can be toxic (Sax, 1975). Since the concentration of bromide is low (about 10%), very much would have to accumulate in order to be toxic. Stop baths, activators, fixers, and hardeners are caustic solutions, and may contain sulfuric acid, boric acid, and chrome alum (White, 1973). Chrome alum is in low concentration in the solution, but is a recognized carcinogen (Sax, 1975).

After developing, the film image must be transferred to the aluminum plate. Plate developing solutions are applied to produce a surface with ink absorbing and ink repelling areas (Rita, 1984, pers. comm.). Developing solutions contain mixtures of aliphatic ketones, amyl acetate, and iso-propanol or n-propanol. All of these solvents are highly flammable (Sax, 1975). The plate is also covered with light sensitive diazo resins, such as 4-diazo-1,1 diphenylamine, or 1-diazo-2-napthanol, and paraformaldehyde (EPA, 1976). Diazo compounds and paraformaldehyde are suspected carcinogens (Sax, 1975).

Printing inks have two main components: fluid ingredients or vehicles, and solid ingredients, the pigments (Gikis et al., 1983). Vehicles are made of resins, oils, and solvents. Resins and oils give body to the ink; solvents aid in blending the vehicle and pigments (Gikis et al., 1983). The pigment is the colorant and image former. Information on the content of pigments is difficult to obtain because manufacturers guard their formulations. Typically, they contain carbon black, lead chromate, and various monoazo and diazo polymers (EPA, 1976). Carbon black, and the monoazo and diazo polymers are suspected carcinogens (Sax, 1975). Lead chromate is a known carcinogen, but there is some doubt by the printers as to whether it is still used in printing inks. At any rate, the inks contain only small amounts of these carcinogens. Generally, inks are handled as non-toxic materials (Gikis et al., 1983).

Offset inks, which are of a pasty consistency, use oils as the vehicle. The solvent content is lower than flexographic or gravure inks, and the pigment content tends to be higher. Some printers in Berkeley use the very low solvent, ultraviolet curing inks; however, these are more expensive. A typical formulation of the sheet-fed offset type is (Gikis et al., 1983):

pigment - 23%
linseed oil - 43%
pthalic alklyd resin - 8%
polyethylene wax - 3%
phenolic modified penta ester of rosin - 15%
ink oil - 5%
drier - 3%

It should be emphasized that this is a general formula, not an exact formulation. Mixed with the ink at the press is a fountain solution containing isopropanol (EPA, 1976), which is flammable (Sax, 1975).

Cleaning solvents and rubber rejuvenators are also hazardous materials. These are maintenance materials used to clean off rollers and blankets, and to keep the rubber soft. Commonly used cleaning solvents are kerosene (flammable and carcinogenic), methyl ethyl ketone (flammable), ethyl acetate (flammable), and xylene (highly toxic and flammable) (EPA, 1976; Sax, 1975).

The inks contain about 10-20% hydrocarbon solvent with about 80% of this evaporating to the air (EPA, 1976). Once the ink dries on the paper, it is not considered a hazardous waste (Gikis et al., 1983).

Any photochemicals that are not recycled can enter the waste water stream. Bromides, small amounts of silver, aliphatic ketones, diazos, isopropanol, and formaldehyde are all potentially hazardous to the environment. But because the quantities that actually need to be disposed of are small, photochemicals are not a big waste problem for Berkeley printers.

Occupational Hazards

The most serious hazard to employees is the emission of hydrocarbons, alcohols and chlorinated hydrocarbons. During press operation, these solvents evaporate from ink, fountain solutions and dampening systems. Periods of maintenance and clean-up are characterized by peak levels of solvent vapors in the breathing zones of workers (Gikis et al., 1983), as they wash the rollers, blankets, and other equipment. This is especially serious in the smaller, less sophisticated shops, such as those in Berkeley, where more manual handling and less extensive ventilation are present.

Because of the wide prevalence of skin contact, dermatitis is the most frequent problem. Since organic solvents dissolve fats and oils, they also remove natural fats and oils from human skin. Chlorinated hydrocarbons are excellent degreasers and can cause dermatitis after only a few exposures (EPA, 1976). Since body fluids are slightly acidic, alkaline solvents such as amyl acetate can cause serious skin burns (EPA, 1976). Most of the organic solvents can be expected to cause dermatitis with enough exposure. Organic solvents, if splashed in the eyes, are irritating at least, and some can cause serious eye injury. Most Berkeley workers wore gloves; however, a few did not. This could cause serious health problems, especially in the case of chlorinated hydrocarbons, which are readily absorbed through the skin.

Besides skin and eye contact with liquid solvents, irritation may result from exposure to solvent vapors. Methyl ethyl ketone, acetone, and ethyl acetate are all local irritants of the mucous membranes (EPA, 1976).

The most potentially serious problem, however, is the depression of the central nervous system resulting from the inhalation of hydrocarbon or alcohol vapors (EPA, 1976). Hydrocarbons, and especially chlorinated hydrocarbons, have a powerful narcotic effect. Dizziness, blurred vision and loss of coordination are a few of the symptoms of this effect. Some of these hydrocarbons and chlorinated hydrocarbons can cause cumulative poisoning. The liver and kidneys are the organs attacked (EPA, 1976).

Although not likely, oral intake should not be overlooked. Swallowing of toxic chemicals may occur to a minor extent when contaminated air is deeply inhaled (EPA, 1976). More serious amounts may be introduced into the body when misted vapors are inhaled, or when food, drink or cigarettes become contaminated by vapors or hands. Although misted vapors are not likely in Berkeley shops, food and cigarette exposure is.

Some of the older printshops in Berkeley still smelt their own lead typeplates. The worker is exposed to lead vapors during the meltdown, and dermally during the clean-up. Lead is a very toxic heavy metal, a suspected carcinogen of the lungs and kidneys, as well as a cumulative poison to the central nervous system (Duffus, 1980). Since most shops have their typeplates made for them, very few workers are exposed to lead.

Environmental Effects

Air emissions are the largest environmental problem of the printing industry. All hydrocarbons, some ketones, and some chlorinated hydrocarbons are photochemically reactive. This means that in the presence of sunlight, these compounds react to form oxidants, which are the main component of photochemical smog. Oxidants are irritating to human lungs and eyes, reduce visibility, are damaging to vegetation, and degrade materials such as nylon, rubber and polyesters.

Larger printers have ventilation control systems to recover emissions by 90% (Gikis et al., 1983). Smaller shops, such as those in Berkeley, have little or no emissions control.

Another potential environmental hazard is the photochemical wastes entering the sewage waste water. These wastes contain a wide variety of chemicals that can be detrimental to water quality and wildlife. Photochemical wastes are acidified solutions of isopropanol, aliphatic ketones, formaldehyde, diazo resins and small amounts of silver. Organic solvents and alcohols can bioaccumulate and are moderately toxic to fish. Silver can also bioaccumulate, and is slightly toxic to fish. The effects of diazo are not well known. Because the entry levels of these chemicals are very low from Berkeley's printers, the environmental risk is not great.

Of the oils and pigments in ink, 90% go on the printed product, which is non-toxic once it dries. Berkeley's printers have very little if any waste ink, and all clean-up residues are retained with the cleaning solvents in the rags.

Conclusion

The printing industry has improved its environmental record dramatically over the last ten years (John Hinton, 1984, pers. comm.). Federal air pollution standards have brought about a reduction in the solvent content of inks. Alcohols have replaced hydrocarbons as ink solvents, and the use of "exempt" solvents, those that do not photochemically react, has increased. Technology has also brought low solvent, ultraviolet curing inks, water-based inks and incinerators to reduce emissions. The use of heavy metals and poly vinyl chloride in ink has also declined (Gikis et al., 1983).

It appears that most Berkeley printers have solved their hazardous waste problems by using small quantities of hazardous materials, and by recycling. Ten years ago, photochemicals and solvents were dumped down the drain, and film and plates were thrown in the trash (John Hinton, 1984, pers. comm.). Today all these materials are recycled, resulting in a cost-efficient and ecologically sound management program. Those printers that do use large quantities of solvents, inks, and photochemicals fall into the large generator category. They must have waste water discharge permits, and must also have ventilation systems with after-burners to reduce solvent missions (John Hinton, 1984, pers. comm.). In Berkeley, sheet-fed offset predominates, instead of gravure and flexography, which are usually roll-fed. The sheet-fed operations are smaller users of inks, solvents, and photochemicals than roll-fed, and the inks themselves contain less solvent.

The only potentially hazardous wastes are photochemical in nature, and small quantities enter the sewer system from Berkeley printers. If enough small printers dump photochemical wastes each month, a pollution problem could develop. Since several small printers are more likely to escape detection than a larger printer, better monitoring is needed at the city level. The exact composition of the waste water effluent from printers should also be determined. Based on the results of the survey, however, it appears that low levels of environmental contaminants enter the sewer, and that no environmental problem is posed.

At the occupational level, long-term studies are needed on the effects of pigments. Although most workers wear gloves for dermal protection, there is some evidence that carbon black can carry pigments into the air in particulate form (EPA, 1976). There should also be a study of the concentrations of airborne solvents in Berkeley's small, poorly ventilated print shops.

Finally, small businesses should be better informed about what hazardous materials and wastes are. Most printers' practices depended on economic reasons, not on knowledge of the laws. If the economics of recycling and conservation of chemicals did not pay, perhaps usage and disposal habits would change.

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