Photographic Processing

Best Management Practices For

Hazardous Materials/Waste Handling

(Updated April 2016)

Best Management Practices (BMPs) should be thought of as "good housekeeping" procedures. In photographic processing facilities, you may have waste streams regulated as hazardous waste by federal and state laws. Many of these waste streams could be considered nonhazardous if properly recycled instead of disposed of in the trash or down the drain. Listed below are typical waste streams, along with procedures to help you comply with these regulations and help reduce the liabilities associated with noncompliance.

PHOTOGRAPHIC INDUSTRY

GENERATION SOURCES AND DISPOSAL OPTIONS

Silver is the element used as the light-sensitizing agent in most photographic materials and is present in photographic fixer solutions as silver thiosulfate complex. The speed, color, and image quality is determined by the quantity of silver used in fabricating the film. During the developing process, silver is released in the fixer and the bleach/fix. In addition, silver is also present in the wash water as a result of being carried from the different processing tanks. Bleach solutions from black and white reversal processing contain silver as soluble silver sulfate, and can also have significant amounts of chromium as dissolved dichromate or chromic ion. The concentration and distribution of silver in the photo processing solutions depends on the type of photo processing system used, method of collection, type of wash, and the amount of film processed per day.

Eventually, the solutions must be replaced, and the used solutions must be disposed of. The used solutions can be stored in containers (DOT approved) and hauled away by commercial hazardous waste haulers, or discharged to a sewer system (Publicly Owned Treatment Works-POTW). If the film processor elects to discharge the "waste" chemicals to a POTW, the "waste" must be treated to reduce the silver content prior to discharge. To receive permission to discharge this type of waste stream, contact your sewer district's "pretreatment officer". Discharges to a septic system will require approval from the Lee County Health Department. This type of disposal is not recommended because of the potential to contaminate onsite property and because these chemicals may destroy the biological process necessary for septic tanks to continue effective operation. It is important you know the difference between a POTW and an onsite septic system in order to meet the requirements for proper disposal.

Several silver recovery treatment technologies have been developed because of various factors: Disposal methods and variables such as geographical location (sewer district) and hazardous waste generator classification, of a particular photo processing lab; Selection of the appropriate method depends on the size of the processing facility, the amount of film processed, the waste disposal or discharge requirements, and the capital available for equipment procurement. Recovering silver provides an additional benefit of being a product to sell.

METHODS OF REDUCING THE VOLUME OF EFFLUENT PROCESSED

1. Use film-processing chemicals which require the least amount of liquid overflow, and have the lowest replenishment rate. Check the manufacturer's Safety Data Sheets (SDS) [formerly Materials Safety Data Sheets (MSDS)] and make comparisons to determine which chemicals will provide the optimum usage time and the least amount of rinse water.

2. Use counter current rinsing, rather than fresh water, at each stage to reduce the amount of discharge. The solutions should be tested frequently to ensure proper chemical content. To increase the effectiveness of this technique, it may be advisable to use squeegees to minimize carryover of contaminants into each rinse stage.

3. Cover processing tanks to reduce evaporation and subsequent need to reconstitute the solution.

4. To reduce the possibility of introducing additional silver into the process solutions or the effluent, thoroughly clean the system, drain lines, sumps, etc. to remove any buildup of deposits which have accumulated over the years.

5. Monitor the effluent to the drain frequently and consistently, and keep records of the observations. Send samples of all solutions to an independent testing lab to ensure an accurate analysis for your process.

METHODS OF MEASURING THE PRESENCE OF SILVER IN FIXER SOLUTIONS

1. *Metal Replacement on Copper* - A clean copper strip is dipped into the fixer effluent; if silver is present, the copper will change color. This method does not indicate the quantity of silver in the solution, only that silver is present. Experienced users, however, are able to judge the relative content based on the appearance of the silver on the copper strip. Material cost is about $1 per test and can be purchased from any metal supplier.

2. *Silver Test Papers* - The fixer effluent will cause the test strip to change colors, depending on the silver content of the fixer. This test is somewhat more comprehensive than the Metal Replacement on Copper test, because of a direct correlation between distinct color changes and silver content in the solution. Material cost is about $2 per test; test papers can be purchased in photo supply shops.

3. *Titration* - This test is used to precisely measure the silver content of the fixer, and must be conducted in a laboratory by a trained technician. Cost per test runs $18-$50.

4. *Atomic Absorption Spectrophotometry* - A very precise method for measuring the silver content of the fixer; used only by larger processors with extensive laboratory facilities. If the solution is sent to a laboratory for testing, the cost per test is $20-$60.

SILVER RECOVERY METHODS

1. *Metallic Replacement* -This process consists of passing the fixer or bleach-fix, which contains silver, through a relatively inexpensive cartridge filled with steel wool. The silver is recovered as sludge. Metallic replacement occurs when the silver solution comes in contact with iron (steel wool). The iron goes into a solution as a dissolved ion, and the silver is reduced to its metallic state and drops to the bottom as a sludge.

   The metallic replacement method is particularly suited to smaller processors due to its low cost *(typically $280-$350 per system, with an annual operating cost of $150-$250). The cartridges are available from several sources, are easy to install, and require low maintenance. Other advantages of this process are: no requirement of electrical power, and silver concentrations in the effluent can be reduced to less than 5 mg/L.

2. *Electroplating* - The fixer is passed through a unit which electrolitically causes the silver in the solution to be plated to cathode as essentially pure silver. The remaining solution may also require further processing by the Metallic Replacement method if residual silver is present.

   There are two basic techniques for installing an electroplating system. A recirculating type of equipment is installed to allow the fixer to pass through the unit on a continuous basis and the recovered solution is reused, or a system processes the fixer outside the loop. Both electroplating methods of silver recovery require the use of considerably more costly equipment than the metallic replacement method. In addition, electrical power, which is converted to direct current, is required to activate the system. *(Cost for a typical system is $3,000-$4,500; annual operating cost runs $75-$250).

4. *Ion Exchange* - Very effective recovery of silver from dilute solutions such as wash water, but it cannot be used to recover silver from fixer or bleach fix. The solution is initially pumped through a column of anion-exchange resin. Further processing is required to recover the silver from the resin by electroplating or precipitation methods. The Ion Exchange method is used primarily where silver discharge must be strictly limited and requires costly equipment *(Typical cost is $6,500 - $7,000 per system; $550 - $770 annual operating costs).

5. *Evaporation / Distillation* - Water is removed from the solution by evaporation, leaving the solid residue behind for disposal or recovery. The evaporated water can be recovered by condensation and disposed of to the POTW or reused. *(Typical system cost is $2,600-$5,900, annual operating cost is $75-$150).

6. *Chemical Precipitation* - Metallic silver and insoluble silver compounds can be precipitated from photo processing solutions with chemical reagents such as sodium borohydride and sodium sulfide. This method of recovering silver requires relatively inexpensive equipment *(typically $165-$350 per system and $50-$100 annually to operate), and is used primarily by manufacturers of photographic supplies, rather than by photo processors.

7. *Reverse Osmosis / Ultra-filtration* - The solution is forced through a semi-permeable membrane under pressure. The water passes through the membrane, while silver

and other dissolved species are collected on one side of the membrane. The sludge containing the silver can be disposed of as hazardous waste, or processed further to recover the silver for resale.

*(Typical costs and annual operating expenses are based on 100 to 200 rolls/day processing. Exact cost may vary).

If you have any questions, please call the Division of Natural Resources Management, Pollution Prevention (P^2) Program at (239) 652-6126.