MANAGEMENT OF PHOTOCHEMICAL WASTES

Source Reduction, Silver Recovery, Safe Substitutes

By Sue Allen

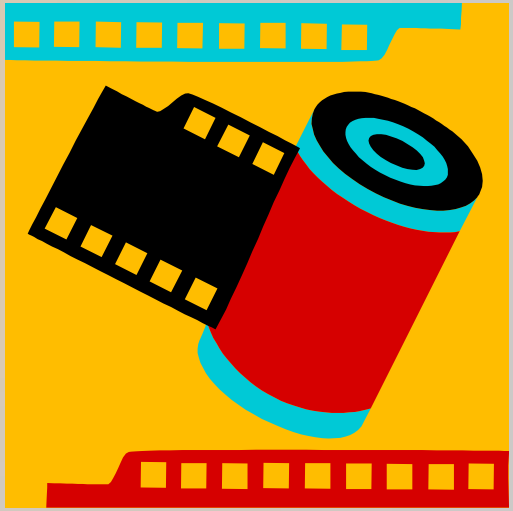
Maryland Dept. of the Environment
Water Management Administration
Underground Injection Control Program

MAJOR PHOTOCHEMICALS

- Photography is very dependent on chemicals.
- Wastewater from the photographic process contains contaminants such as: hydroquinine, sodium sulfite, silver, mercuric chloride, cadmium, ferrocyanide, acids, and formaldehyde.
- The types of wastes include: process bath wastes, color developer wastes, bleach, fixer and fixer wastes. All are toxic and highly alkaline.
- Laws affecting photoprocessing include the Safe Water Drinking Act and the Toxic Substances Control Act.

SILVER EXPOSURE IN BIOSPHERE

- Silver is a rare but naturally occurring metal deposited as mineral ore, extracted from the main ore, Argentite.
- It is recovered as a by-product from smelting nickel or copper ores and from platinum & gold deposits.
- Sources of silver include emissions from smelting operations, manufacture & disposal of photographic /electrical supplies, coal combustion & cloud seeding.
- Sorption is the main process that controls silver's entry into water & its movement in soils.



WASTE DISPOSAL OPTIONS

- About 100 million gallons of silver-bearing wastewaters are produced annually.
- Materials that leach more than 5 mg/L of silver are classified hazardous waste.
- Most POTW's can tolerate and treat photo wastewaters - if the volumes and concentrations of contaminants are not too high.
- Local sewer authorities regulate concentrations & volumes per day of chemicals released into sewer systems.

SILVER-BEARING WASTE

- Silver in photoprocessing waste is less toxic than “free” silver which can kill aquatic organisms.
- Silver thiosulfate is the dominant silver compound in photoprocessing effluents.
- High concentrations of organic & sulfur-based materials in municipal wastewater treatment systems ensure that any active silver materials are combined into sludge.

SILVER-BEARING WASTE

- After silver is discharged into natural waters, it is found tightly-bound in sediments, where it remains and not released into the water column.
- Silver nitrate can cause skin, eye, and respiratory irritation.
- Argyria, a condition characterized by bluish-gray pigmentation of the skin, mucous membranes and eyes, is a major effect resulting from long-term chronic exposure to silver.

ONSITE SEWAGE DISPOSAL (SEPTIC SYSTEM)

- Subsurface disposal systems are designed to manage domestic wastes.
- Septic systems do not have the ability to properly treat photographic effluents since septic systems operate with anaerobic biological treatment.
- MDE does not recommend discharging photoprocessing chemicals into septic systems because these chemicals upset the functioning of the systems and adversely affect nearby underground drinking water sources.

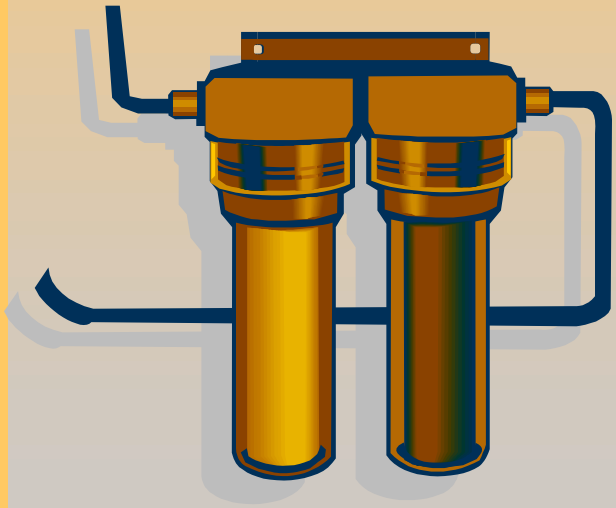
CODE OF MANAGEMENT PRACTICE

- The Code of Management Practice for Silver Dischargers is a voluntary set of recommendations on technology, equipment, & procedures for controlling silver discharges and preventing pollution.
- The purpose is to develop a consensus among localities and photo-processing silver dischargers to reduce regulatory burdens and costs for municipalities and small businesses.
- The Code involves the use of recovery and equipment options best suited to a facility, to enhance silver recovery & track the monitoring processes for effectiveness.
- Silver has a secondary drinking water standard of 0.1 parts per million (ppm).

SILVER RECOVERY

- Silver Recovery harvests silver from photoprocessing solutions.
- There are several ways to recover silver, depending on the operation size, the concentration of silver in the effluent, and the silver discharge limits for the local POTW.
- Concentrations of silver in used fixer usually exceeds allowable limits for discharge to municipal water systems.
- The silver recovery process controls laboratory costs and maintains the lab's regulatory compliance.

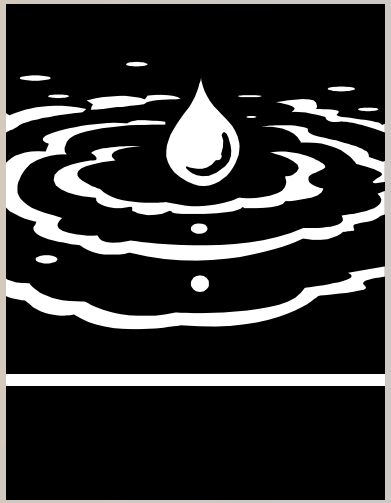
TYPES OF SILVER RECOVERY



- **Metallic Replacement** involves an active solid metal, such as iron, contacting a solution containing dissolved ions of a less active metal.
- **Electrolytic Recovery** applies a direct current across 2 electrodes in a silver-bearing solution. Metallic silver deposits on the cathode.
- **Chemical Precipitation** mixes a precipitation agent with silver-bearing wastewater in a batch reaction tank with pH control. Solid particles are formed, settle before filtering, and are sent to a silver refiner.

SILVER RECOVERY FROM RINSE WATER

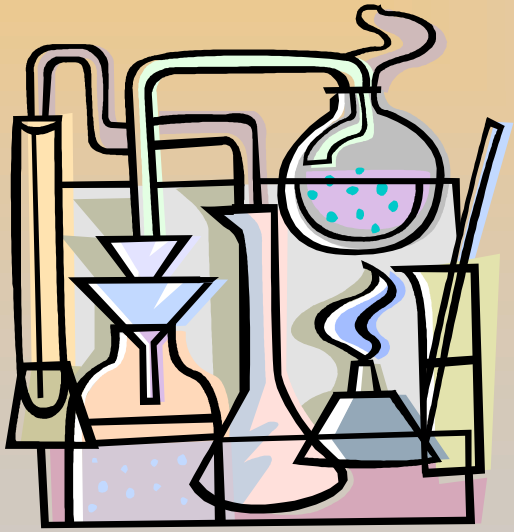
- **Ion Exchange** is the reversible exchange of ions between a solid resin and a liquid. It can recover up to 98% of silver.
- **Reverse Osmosis** has the wastewater flow under pressure over the surface of a selectively permeable membrane. Water molecules pass through the membrane, and other constituents are left behind, recovering 90 % of the silver thiosulfate.



SILVER RECOVERY OPTIONS

- Developer/fixer disposal can be handled through an off-site silver reclamation facility, licensed to accept hazmats.
- Operate your own silver recovery unit. This unit must be operated under certain regulations. Ensure that the silver concentrations in your system are acceptable to the local sewer system.

BEST MANAGEMENT TECHNIQUES



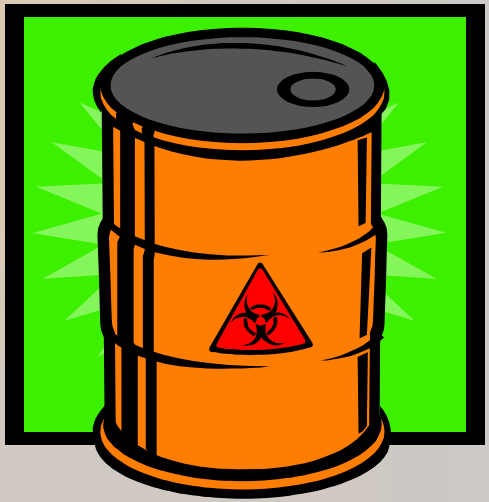
- Seal all floor drains connected to the sewer or storm drains by production area.
- Any solutions touched by developer must be put in hazmat. receptacle for pick-up by licensed hauler.
- Use squeegees to wipe excess from films and papers. This saves $$ & chemical quantities.
- Install secondary containment around all machines.
- Keep waste fluid segregated for reuse, recycling or trt.

BEST MANAGEMENT TECHNIQUES

- Floating lids on replenisher tanks reduce oxidation, evaporation & contamination from dirt.
- Replace highly toxic developers, such as catechol, chlorquinol, and pyrogallo with less toxic ones, such as phenidone.
- Donate unemulsified inks to school or public agencies.

BEST MANAGEMENT TECHNIQUES

- Clean up spills at once. Use absorbent materials to confine any fluids.
- Replace solvent-based plate-making systems with water-bases ones.
- Reduce amount of waste rinse water by using countercurrent rinse tanks.
- Install automatic ink levelers to keep ink fountains at optimal level for good print quality in large web presses.



PHOTOCHEMICAL RECYCLING

- Choose inks & cleaning solutions that are non-toxic.
- Avoid halogenated compounds, petroleum-based, or phenol cleaners.
- Recycle spent fixer, solvents, waste ink.
- Strip “goldenrod” from negatives and used metal plates & accumulate for pick-up by a licensed hauler.
- Accumulate “chromoliths” for recycling.

SAFE SUBSTITUTES

- Use soybean, walnut, or vegetable oil-based inks for lithography printing. Water-base inks can be used for screen printing.
- Reduce concentration of Isopropyl Alcohol (IPA) with a fountain solution with low IPA or switch to low-VOC substitutes.
- Use soap solutions when possible. Solvents should be used only for cleaning inks & oils.
- Some specially made blanket washes & acetic acid-based solvents, with less hazmats, are now available.
- Some small solvent recovery systems are on market, able to accommodate many medium-large printers.

PHOTORECYCLING NEWS

* Washless minilabs use a stabilizer instead of washwater, recovering silver effluent and discharging it only to a municipal secondary treatment system.
* Digital cameras now rival conventional photography. They recycle by reducing size & run on fewer batteries. Some companies remove lead from lenses, cadmium from sensors, & mercury from displays.
* The disposable camera is the most recycled consumer product. Polystyrene covers & viewfinders are grinded down into new camera components and lens acrylic is made into toothbrushes.
* One company extracts 99% of the silver and other toxic heavy metals from used photo liquids to produce a liquid fertilizer.

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