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# Silver Recovery from Photographic and Imaging Wastes

## Introduction

The processing of photographic and radiographic (x-ray) image films and papers is a major source of silver-containing waste discharges in the Air Force. The Air Force has been recovering silver from these waste streams for many years. Recovering silver from image processing wastes helps offset the costs associated with image processing and aids in achieving compliance with regulatory limits on silver concentrations in discharges. Silver recovery also conserves a non-renewable precious metal resource.

This Fact Sheet addresses the environmental effects of silver, principal types of silver-containing photographic wastes, applicable environmental regulations, and commonly available silver recovery technologies, including support services provided by the Defense Reutilization and Marketing Service (DRMS). Potential generators of photographic and imaging wastes are hospitals, dental clinics, photographic laboratories, printing plants, microfilm and microfiche producing facilities, and hobby craft shops.

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## About Silver

Silver is a naturally occurring element and a precious metal. Forty percent of all silver used in the United States is used in photographic and imaging materials (approximately 70 million troy ounces/year). Silver is unique in its ability to react to light and produce images in applications such as photography and radiography (x-rays). No other metallic element possesses these properties. Silver is released from photographic films, papers, and plates during development and printing processes and can be successfully recovered from waste streams (i.e., used processing chemicals) for reuse.

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## Environmental Effects of Silver

Silver is released from image processing operations as silver thiosulfate, which degrades in the presence of oxygen to primarily silver sulfide, and to a much lesser extent, silver halide complexes. These compounds are non-toxic to plants and organisms, very stable, insoluble, and immobile in the environment. Silver is not significantly taken up by plants and does not bioaccumulate.

In January 1991, the Environmental Protection Agency (EPA) deleted the interim primary maximum contaminant level (MCL) for silver, established under the Safe Drinking Water Act (SDWA), based on the finding that silver posed no adverse human health effects. However, silver continues to be designated a "priority pollutant" under the Clean Water Act. In addition, under the Resource Conservation and Recovery Act (RCRA), silver is listed as an indicator that a solid waste is hazardous (toxicity characteristic) when present in leachate at a concentration of 5.0 milligrams per liter or greater.

Unlike silver sulfides and halides, the hydrated or "free" silver ion is potentially toxic to aquatic organisms. However, this form of silver is rarely found in the environment because it combines so readily to form non-toxic complexes with common organic materials found in natural waters. The "free" form of silver is not a normal component of photographic and imaging waste streams.

Although silver in its most common forms has no adverse human health effects and no apparent adverse environmental effects, because it is a precious metal capable of being reclaimed and reused, it is economically (and environmentally) sound to do so.

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## Types of Silver-Containing Photographic Wastes

When light-sensitive silver halide compounds in photographic films or print papers are exposed to light, they undergo a chemical change and form a "latent" image (not visible to the naked eye). The latent image is amplified in a chemical bath during the "development" process and is stabilized during the "fixing" process. The exposed silver halides are chemically reduced to elemental silver (blackened) during the development process, thereby making the image visible on the film or paper. The unexposed, and therefore undeveloped, silver halides are converted during the fixing process to water-soluble compounds. The unexposed silver compounds are then dissolved from the film/paper and are found in greatest concentration in used fixer solutions, and in lesser quantities in rinse waters. (Typically, fresh photo processing solutions contain no silver, and insignificant amounts of silver are found in used developer solutions.) Nearly all the silver in imaging wastes is in the form of silver thiosulfate complexes, which are non-toxic and highly stable in the environment.

Discarded imaging films and papers are also silver-containing wastes. Since they are dry solid wastes, they are easily managed and are generally sold directly to a contractor for silver recovery. This fact sheet does not address technologies for recovering silver directly from imaging films or papers.

## Fixer Solutions

In a typical film processing operation, the fixer bath is continuously augmented with fresh fixer solution to maintain its quality and strength. Consequently, there is a continuous overflow discharge of used fixer solution from the fixer bath. The concentration of silver compounds suspended in the used fixer bath discharge can vary greatly depending on the type and amount of film being processed, but frequently exceeds 5,000 parts per million (ppm). Because of this high silver concentration, silver recovery from fixer solutions is very cost effective.

## Rinse Waters

When developed images (films or papers) are moved from the fixer bath to the rinse, they still carry a small amount of silver, which is removed by the rinse water. Rinse waters contain low concentrations of silver ranging from less than 1 ppm to as high as 200 ppm. Although there is little economic benefit to recovering silver from rinse water, environmental regulations may prohibit discharge of untreated rinse water to treatment works or the environment if the silver concentration exceeds specified concentrations.

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## Regulation of Imaging Waste Streams and Discharges

Silver-containing effluents discharged from image development processes or from silver recovery equipment are subject to regulation depending on how and where they are discharged, and how much pre-treatment (silver recovery) it has undergone.

If the treated or untreated waste stream is discharged directly to a storm sewer or surface water body as a process wastewater, it is regulated as a point source under the Clean Water Act (CWA) and is subject to permitting under the National Pollutant Discharge Elimination System (NPDES). A NPDES permit allows the discharge of treated or untreated wastewater to surface water bodies provided the effluent meets permit-specific quality standards. Silver containing waste streams may require pre-treatment in order to meet NPDES target concentrations for silver (typically 5 ppm or less) and other regulated contaminants that may be present.

If the treated or untreated waste stream is discharged to a Publicly or Federally Owned Treatment Works (POTW/FOTW), it will have to meet pretreatment requirements as determined by the accepting Treatment Works. Discharges from Treatment Works to surface water bodies are subject to NPDES permit requirements. An Air Force installation, whether it operates its own Treatment Works or discharges to a nearby POTW, must ensure its



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