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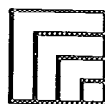
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Silver Recovery Techniques

Technical Report

AIIM TR4-1989



AIIM

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Technical Report for Information and Image Management —

Silver Recovery Techniques

Association for Information and Image Management

This technical report covers the economics and techniques of recovering silver from used photographic processing solutions. Included are vendors of equipment and supplies, refiners of recovered silver, and a suggested reading list of other sources of information.

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Foreword

Silver recovery technology has been available for more than 50 years and has been the subject of many articles and publications. This report is a revision of TR4-1982 published by the National Micrographics Association, now AIIM. This updated version is a current and comprehensive publication specifically written for the micrographics community.

Suggestions for improving the technical report should be sent to the Chairman, AIIM Standards Board, 1100 Wayne Avenue, Suite 1100, Silver Spring, Maryland 20910. The AIIM Standards Board had the following members at the time it approved this technical report:

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The earlier version of this report was prepared by the NMA Ecology Standards Committee, C6, Chaired by Kenneth M. Smith of DuPont Company.

Technical Report for Information and Image Management—Silver Recovery Techniques, AIIM TR4-1989

1 Introduction

Poets have spoken of silver and its beauty for thousands of years. Men have betrayed and killed for it. Financiers hoard it. Modern technology depends on it for applications in medicine, electronics, chemical processes, and photography. Front page stories of wild fluctuations in the price of silver have dramatized the importance of conserving this valuable natural resource. For whatever happens to the price of silver, there is only so much of it on the planet and every year more silver is consumed than mined. The recovery of silver from scrap film and from spent photographic processing solutions is vital in redressing the balance. At least one-third of all the silver consumed each year goes into photographic products. As the largest single user of silver, the photographic industry is in the best position of all to participate in the recycling process and thereby ensure an adequate supply.

Another reason to recover silver is to meet environmental regulations. Silver is classified as a "priority pollutant" and toxic metal by the Environmental Protection Agency (EPA). In addition, most federal and state environmental agencies have assumed that all chemical species of silver are toxic despite a growing body of scientific evidence to the contrary.¹ Many municipalities have established sewer codes restricting the concentration of total silver in waste water discharges to a few parts per million or less. If the sewer code is exceeded, one must consider silver recovery from fixers, bleaches (reversal processing only), or wash water. The type of silver recovery technology employed is often dependent upon the silver limitation which must be met. Off-site disposal of processing solutions may have to be considered in some extreme cases.

Technology for recovering silver from used fixer has been around for decades and is widely available. Silver recovery from reversal bleaches and wash water is more difficult and requires special handling. Still another compelling reason to recover silver is economics. Silver recovery was profitable when the metal was selling for less than \$3 per troy ounce. We are not likely to see such low prices again, and properly sized recovery equipment is able to pay for itself in a short time.

Before entering a silver recovery program, first to try to answer a few questions. Many microfilmmers can legitimately ask whether they use enough fixer to justify their involvement with silver recovery methods. If various companies do venture into such activities, should they recover silver themselves or is it better to have someone else do it?

Initially, the most important thing is to become acquainted with the basics of silver recovery to determine the approach best suited to a particular situation. If there are unanswered questions, help is available from a number of sources. These include silver service companies, firms supplying film and chemicals, silver recovery equipment manufacturers, and their dealers.

2 Sources of Silver

In the micrographics industry, silver may be recovered from two main sources: exhausted processing solutions and processed films or papers. When film is wet-processed, as much as 70 percent of the silver in the emulsion layer is removed and remains in the processing solutions. The rest of the silver stays on the film to form the image. When film or paper is no longer required for records purposes, it may have substantial value. Variables that influence the value of the scrap film include the type of product, the size of the image area, polarity, the quantity available, and the market price of silver at the time of refining. The only way to determine the true value of the film is to assay a representative sample. The other source of silver is the spent processing solutions. In conventional microfilm processing, the greatest percentage of recoverable silver is in the fixing bath. Photographic fixers convert unexposed, undeveloped silver halide to soluble silver compounds which diffuse out of the emulsion layers.

In black-and-white reversal processing, most of the silver usually remains on the film. Silver that is removed is found in the bleach and fixer. However, the concentration may be too low, and the extraction technique too time consuming, to be economical for most microfilm installations. Silver also is found in wash water, but usually in concentrations too low for profitable recovery. However, silver recovery may be necessary to meet municipal regulatory requirements.

Micrographic films and papers that do not contain silver include diazo, vesicular, and most electrostatic materials.

3 Some General Considerations

3.1 General. If silver recovery is not required to meet municipal sewer code regulations, it should be recovered to conserve a valuable resource. In addition, the economics of silver recovery should be addressed. To find out how much silver is potentially available from the fixer that is being consumed, you must identify the usage rate of the fixer and the silver concentration, then perform this equation:

$$\begin{aligned} &\text{Silver concentration in troy oz/gallon} \\ &\times \text{gallon/week} = \text{troy oz of silver/week} \end{aligned}$$

¹An Eastman Kodak Company technical report, Silver and the Environment, reviews the environmental chemistry and environmental toxicology of silver.

The concentration can be determined inhouse with silver test paper (see Section 6) or by a service company, equipment vendor, or commercial analytical laboratory that can do a chemical analysis. Care should be taken to ensure that the sample of used fixer is representative of the process.

The next step is to find out the current market price for silver. This is given in the commodities listings in the *Wall Street Journal* and in the *New York Times* under the heading "Cash Prices."

Silver recovery may be profitable even if the potential return is less than \$20 to \$25 per week. This takes into account the fact that the quoted market price is for bullion grade silver and that, for reasons to be discussed later, a sale of small amounts of impure silver seldom realizes more than 50 percent of the market price. If silver recovery is economically feasible, two options are available:

- (1) Sell the seasoned fixer; or
- (2) Recover the silver inhouse, either with a metallic replacement cartridge or an electrolytic unit. Both techniques can be employed with equipment purchased directly by the microfilmer or with the equipment installed and serviced by a service company.

3.2 Selling Seasoned Fixer. The small user will have to save the spent fixer until enough is accumulated to be of interest to a potential buyer. This is discussed in Section 7.

3.3 Inhouse Silver Recovery. If the fixer volume is large enough, no money at all needs to be invested in equipment. There are silver service companies that will come to the plant, install a system on the processor, monitor it, then take away the recovered silver and use it to pay for the system. The silver service company bears the cost of the equipment and the people needed to monitor the program, so it will charge a percentage of the recovered silver to cover its costs and profits. This results in some mutual incentive for both the processing organization and the silver service company to operate an efficient recovery program. However, only 50 percent of the market price for the recovered silver may be received.

On the other hand, a properly managed silver recovery system will yield a higher dollar return when the silver is sold and, in the long run, it might provide a higher return on investment. This is a question answered after comparing silver service company proposals with the estimated cost of purchasing and operating equipment inhouse. Shipping, assaying, and refining charges are always involved in the selling of recovered silver. This subject is discussed in more detail in Section 7.

If the decision is made to buy equipment, the choice then must be made between metallic replacement and electrolytic plating devices. These techniques, with their

advantages and disadvantages, are described in Section 4. Appendix B provides a listing of manufacturers of equipment for silver recovery. This is not a complete listing or an endorsement of their products.

4 Inhouse Silver Recovery Methods

4.1 General. The purpose of this section is to review the methods of silver recovery as they apply today to the micrographics industry and the typical micrographics processor. A large amount of information has been published on many aspects of silver recovery. In particular, both Eastman Kodak Company and E.I. DuPont de Nemours & Company have published information on silver recovery which can be very helpful to micrographics processors. Much of the information in this section on silver recovery methods is adapted from Kodak and DuPont sources. (See Appendix E for references.)

The weight of silver is usually calculated in troy ounces or grams. The volume of fixer, developer, and wash water solutions is often discussed in metric measures. Therefore, a table of conversion factors is presented in Appendix A to assist in understanding and using various methods of liquid and weight measurements.

There are three major methods of recovering silver from photographic materials and solutions. They are:

- (1) Metallic replacement (steel wool cartridge);
- (2) Electrolytic plating; and
- (3) Recycling scrap film and paper.

Several other silver recovery methods are also available, but are not widely used. They are described in Section 4.4.

4.2 Metallic Replacement. The metallic replacement method uses a cartridge (usually plastic) which is filled with steel wool, iron wire screen, or iron particles. The tubes located in the lid are the inlet and outlet connections for fixer flow. As silver-laden fixer flows through the cartridge, the iron in the cartridge exchanges places with the silver fixer. The silver then drops to the bottom of the cartridge as a sludge, and the iron-laden fixer is carried out of the cartridge and down the drain. Figure 1 shows a cross section of a typical metallic replacement cartridge.

The advantages of the metallic replacement cartridge are:

- (1) Low cost;
- (2) Easy to install;
- (3) No moving parts—no electrical connection required;
- (4) Will reduce the fixer silver concentration to 20 milligrams per liter or less;