PROCESS MONITORING

Z-129G
$2.00

RECOVERING SILVER FROM PROCESSES USING
KODAK EKTACHROME R-3 Chemicals

You can recover silver from KODAK EKTACHROME R-3 Bleach-Fix II and Replenisher with electrolytic recovery cells or chemical recovery cartridges. You can also use either of these devices to recover silver carried over into the first tank of the final wash.

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HOW CAN I GET THE MOST EFFICIENT SILVER RECOVERY FROM MY PROCESS?

For the most efficient recovery with either method, you will need to limit the amount of silver carried out of the bleach-fix and the low-flow wash. If your processor has at least three final wash tanks, you can increase the efficiency of silver recovery by converting the first tank of the final wash to a low-flow wash.

Bleach-Fix

Install a set of double-blade squeegees at the entry into the first bleach-fix tank and at the exit of the last bleach-fix tank to limit solution carry-over. Replenish the bleach-fix at a rate of 20.4 millilitres per square foot (220 millilitres per square metre) of paper. Arrange the tanks so that the replenisher enters the last tank and the solution flow through the tanks is countercurrent to the direction of paper travel. The solution overflow is from the first tank.

Monitor the silver concentration in the bleach-fix regularly. The silver concentration in Tank A of the bleachfix should be in the range of 4.5 to 7.0 grams per litre. A lower silver content will result in reduced plating efficiency. Higher silver levels cause yellow stain in the paper. An easy way to check the silver concentration is with KODAK Silver Estimating Test Papers. Silver content is controlled primarily by the bleach-fix replenishment rate and by the entry and exit squeegees.

Low-Flow Wash

To recover silver from the wash following the bleach-fix, you will need to use a low-flow wash. A low-flow wash concentrates the silver in the wash so that it is more easily recovered. On processors with a final wash that consists of three or more tanks, separate the plumbing and the replenishment of the first tank from the other tanks. Replenish the first tank at a much lower rate: 14.9 mL/ft^2 (160 mL/m^2). Use a precise metering device. This low-flow wash will collect silver normally lost from the wash. Install a set of double-blade squeegees at the low-flow wash exit to reduce solution carry-over. Collect the combined overflow of the bleach-fix and the low-flow wash in a storage tank for treatment with an electrolytic cell or chemical recovery cartridge. If a fungus grows on the surface of the solution in the collection tank, remove it and add a small amount of thymol to prevent further growth.

If your processor has only two tanks for the third wash, *do not* use a low-flow wash. The silver yield with these processors will be significantly lower because of solution carry-over.

ELECTROLYTIC SILVER RECOVERY

For electrolytic silver recovery, your setup should consist of a holding tank for the solution to be desilvered, a high-density electrolytic cell with one or more rotating cathodes, a pump to provide continuous recirculation from the holding tank through the cell, and a power device.

A high-current-density electrolytic silver-recovery unit is required due to the simultaneous reduction at the cathode of silver and iron III. When current is not flowing, you will need to separate the bleach-fix solution from the plated cathode to prevent dissolving the silver. Draining the solution from the cell is the most convenient way to do this. We do not recommend regeneration and reuse of the desilvered bleach-fix.

Treat the solution in consistent batch sizes so that the total electrolysis time and the amounts of the chemical additions will be the same for each batch.

With electrolytic silver recovery you can reduce the silver concentration of the solution to less than 25 milligrams per litre. Silver losses as a result of carry-over will be approximately 2 percent from both the desilvered bleach-fix and the final wash. Most of this is recoverable by using a chemical recovery cartridge after the electrolytic unit.

WHAT ARE THE CHARACTERISTICS OF ELECTROLYTIC SILVER-RECOVERY UNITS?

The capacity of an electrolytic silver-recovery unit can be expressed in terms of the amount of silver plated during a normal working day. If you consider that an electrolytic unit works for a maximum of 20 hours per day, allowing for the time required for loading and unloading, you can calculate the performance by this equation:

$$Q = 20 \times R$$

Where R = recovery rate in grams per hour

Choose a model with performance characteristics that best match the amount of paper processed.

Electrical Factors

A large variety of high-current-density electrolytic silver-recovery units are available. The capacity and control features of these units differ. The nominal capacity claimed by the manufacturer is expressed as grams of plated silver per hour of electrolysis. As a rule, nominal capacity is about 120 grams per hour for the larger models and 30 grams per hour for smaller models. The capacity of the unit is determined by its plating current measured in amperes. Control of the current is important. With too little current, less silver will plate out. With too much current, the thiosulfate may break down to form sulfide ion, lowering the purity of the silver.

The solution capacity and the number of controls on a unit affect the price. The inexpensive units may have an on-off switch as the only means for current control. This is adequate if the process is always in good control, the process load is consistent, and a reliable person monitors the process. Most units have a variable-current control and a meter to indicate plating current in the solution. The plating current increases gradually during electrolysis. With units that have a current controller, you don't have to change the setting to adjust for the current shift. To set the proper plating current, use this formula:

$$I = 1.25 \times C$$

Where I = plating current
C = nominal capacity as grams of silver per hour

Chemical Factors

The higher the pH, the higher the current efficiency (recovery rate). The pH of the solution should be 7.2 or higher for the most efficient recovery. The pH of the combined overflow will usually be at this level or higher, so a routine check of pH is not normally required if the processor has a utilization of at least 10 percent. If the utilization is less than 10 percent, the pH may fall below 7.2. Adjust the pH to 7.2 or higher before electrolysis. For a given iron concentration in the bleach-fix, the higher the silver content, the higher the current efficiency. The silver concentration of Tank 1 of the bleach-fix must be maintained in a well-defined range.

Sodium sulfite prevents sulfurization, which results in blackening of the silver plate, decomposition of the thiosulfate, and sulfur precipitation. A noticeable amount of sulfite is consumed during electrolysis. You will need to add about 10 grams per litre of anhydrous sodium sulfite to the solution before electrolysis. Pour the dry material into the cell slowly while the cathodes are rotating and the solution is recirculating. The sulfite will also raise the solution pH. You can experiment with the level of sulfite addition, but be careful about losing too much sulfite from the electrolyzed solution.

HOW DO I USE AN ELECTROLYTIC-RECOVERY CELL WITH MY PROCESS?

Carefully follow the operating instructions provided with the unit. Pump a convenient volume of solution from the collection tank to the holding tank. Since the solution will not be regenerated, there is no need to use a filter on the unit's recirculation system. Clean the holding tank at regular intervals.

The efficiency of electrolysis depends on the adhesion of the silver plate. Before starting, make sure the cathode is perfectly clean. On models with a stainless-steel cathode, you may need to sandblast the cathode to provide a rougher surface. Many machine shops and electroplating shops perform this simple operation. After sandblasting, thoroughly clean the cathode with scouring powder and a nonmetallic cleaning pad. *Do not* touch the clean cathode surface.

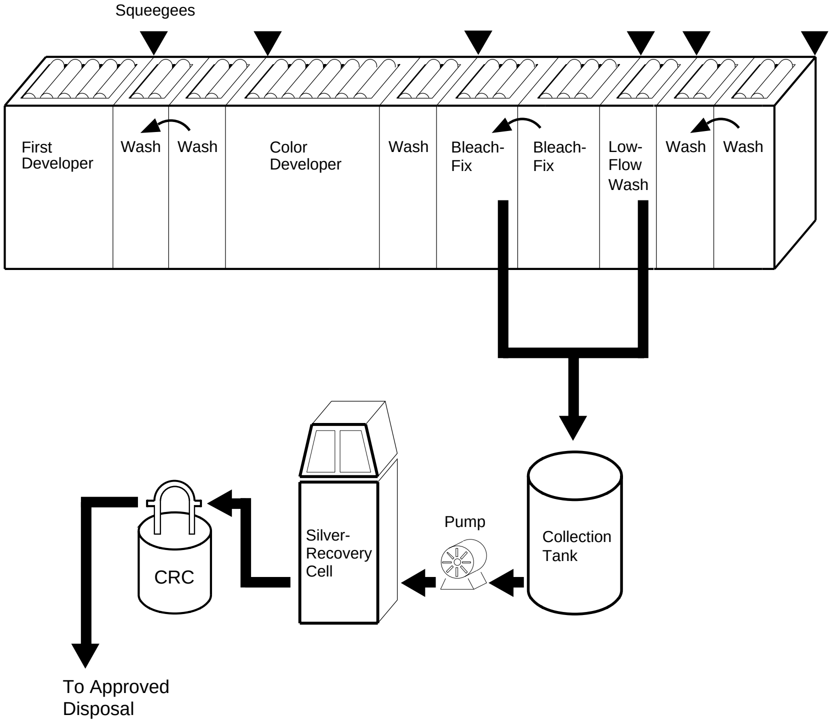

Figure 1

Setup for Silver Recovery with an Electrolytic-Recovery Unit

After you install the cathode, slowly add 10 grams of sodium sulfite per litre of solution, with the cathode rotating and with the solution recirculating between the holding tank and the cell. Also, if you start with a clean, unplated cathode, add 2 grams of potassium iodide per litre to improve plate adhesion.

Determine the starting plating current by using the equation given on page 3. For smaller-capacity units (about 30 grams per hour), an acceptable starting current is in the range of 60 to 70 amperes. Some recovery-unit manuals may state that electrolysis should be at significantly reduced plating current for the first hour; for optimum plate adhesion *do not* follow these instructions for Process R-3.

During electrolysis, monitor the silver concentration to determine the total electrolysis time needed. KODAK Silver Estimating Test Papers are a simple means of checking the silver concentration. You can desilver the solution to a silver concentration as low as 0.2 to 0.5 grams per litre. Desilvering below this level will cause sulfide to form.

During electrolysis, current intensity will increase as the solution temperature increases. The solution temperature depends on the volume of the solution, the current intensity, and the ambient temperature. In warm weather in a non-air-conditioned lab, the temperature can rise to 40°C (104°F) or higher. If the solution temperature gets too high, current efficiency will be reduced. You may need to use some means of cooling to maintain a temperature that will keep the current efficiency in the proper operating range.

The silver plate will adhere well to a properly cleaned cathode. However, dendrites of silver may form, especially at the top and bottom edges of the cathode. As the dendrites grow, they may cause increased agitation and flooding within the cell. Remove these formations after each batch to avoid that problem.

During electrolysis, the rapidly rotating cathode may cause foaming of the solution in the cell. If this continues, foam may also form in the holding tank. Adding a small amount of KODAK Defoamer to the cell during electrolysis will reduce any foaming.

Remove the silver plate from the cathode after desilvering approximately 10 batches. Clean the cathode before reuse.

Treating the Desilvered Solution

After electrolysis, pass the desilvered solution through a chemical recovery cartridge (steel-wool cartridge) to recover the remaining silver and reduce the amount discharged to the sewer. If you use a KODAK Chemical Recovery Cartridge, Model II, pump the solution through at a flow rate of 100 millilitres per minute.

Conditions that Affect the Recovery Rate

To get the most out of your silver-recovery system, consider these factors:

Bleach-Fix Replenishment Rate—If the bleach-fix replenishment rate is too high, the silver content in the bleach-fix tank will be too low for good plating efficiency.

Low-Flow Wash—If the flow rate of the low-flow wash is too high, it will increase the volume of solution to be electrolyzed. That will dilute the solution and produce a loss in plating efficiency. It may also require greater storage capacity.

You can separate the bleach-fix and low-flow wash overflows and electrolytically desilver the bleach-fix by itself. The recovery rate will increase but the yield will decrease. To treat the separate low-flow wash, you will need to use a chemical recovery cartridge.

The low-flow wash contains about 8 percent of the total silver available for recovery. Therefore, if you treat the bleach-fix and the low-flow wash separately, the amount of silver that you will be able to recover from the bleach-fix alone can’t be higher than 88 percent.

Silver Content—If silver content is measured against electrolysis time, the recovery rate drops significantly at a particular silver concentration called the transition point. This concentration is usually in the range of 0.5 to 1.0 grams of silver per litre. In other words, you can stop electrolysis at that point to obtain the best recovery rate, but you will sacrifice silver yield.

Hypo (Thiosulfate) Concentration—The recovery rate increases with increasing concentration of ammonium thiosulfate. Adding 20 to 40 mL of ammonium thiosulfate per litre of solution will also be helpful if you electrolytically desilver to a very low residual silver concentration (0.1 g/L).

Solution pH—The pH should be 7.2 or higher. If you must adjust it, use ammonium hydroxide. Adding ammonia solution to raise the pH from 7.2 to 8.4 increases the recovery rate by 50 percent. However, the ammonia fumes may be severe enough to require more exhaust capacity.

Plate Adhesion—Depending on your electrolytic equipment and on the process solutions being treated, you may have some slight plate-adhesion problems. If this happens, you can improve plate adhesion by doing the following:

- Sandblast stainless-steel cathodes to roughen the surface.
- Use 3 grams per litre of potassium iodide (instead of the recommended 2 grams per litre), and dissolve it in 30 millilitres of ammonium thiosulfate per litre of electrolyzed solution. Slowly add the potassium iodide solution to the solution to be electrolyzed. If your equipment permits, add it to the cell with the cathode rotating and the solution recirculating.

Electrical Contacts—Poor electrical contacts adversely affect the electrical efficiency. Check the contacts periodically.

Electrolysis of Mixed Bleach-Fix Solutions—You can mix Process R-3 bleach-fix and low-flow wash overflow with the following solutions from other processes:

- Process RA-4 bleach-fix and Process RA-4 bleach-fix RT overflow
- Process RA-4 bleach-fix NR plus low-flow wash
- Process EP-2 bleach-fix and Process EP-2 bleach-fix RT overflow
- Process EP-2 bleach-fix NR plus low-flow wash
- Process C-41 fixer after desilvering in a low-current-density cell
- Black-and-white fixers

The Process EP-2 bleach-fix NR overflow can substantially improve the current efficiency because of its very favorable silver-to-iron ratio. Fixers are also beneficial because they increase the hypo concentration.

Maintenance

Carefully follow the equipment maintenance schedule recommended by the manufacturer of the electrolytic unit. Failure to maintain the unit properly may adversely affect performance.

Safety Precautions

Although the plating current is high, the direct-current voltage is usually low (probably less than 5 volts), so there should be no danger of serious electrical shock. However, as a precaution, avoid making contact between the solution or an electrical path of the recovery unit and a ground during electrolysis.

CHEMICAL RECOVERY CARTRIDGES

Chemical recovery cartridges recover silver by means of metallic replacement. With metallic replacement, a more active metal replaces a less active metal in solution. Metal ions, such as those of zinc, iron, and aluminum, can replace silver ions in a solution. Most chemical recovery cartridges, such as KODAK Chemical Recovery Cartridges, use iron in the form of steel wool to replace the silver

The silver thiosulfate complex that is formed during the fixing step of a photographic process contains the silver ion recovered by the steel wool. The reaction that takes place is expressed by the following equation:

$$2Ag(S_2O_3)_2^{-3} + Fe \qquad 2Ag + Fe^{+2} + 4(S_2O_3)^{-2}$$

The silver (Ag) is separated from the silver thiosulfate complex, with iron (Fe) taking its place. The silver collects in the cartridge as a metallic sludge. Cartridge performance and silver yield are directly affected by the successful completion of this chemical reaction. A typical setup for using chemical recovery cartridges is shown in Figure 2.

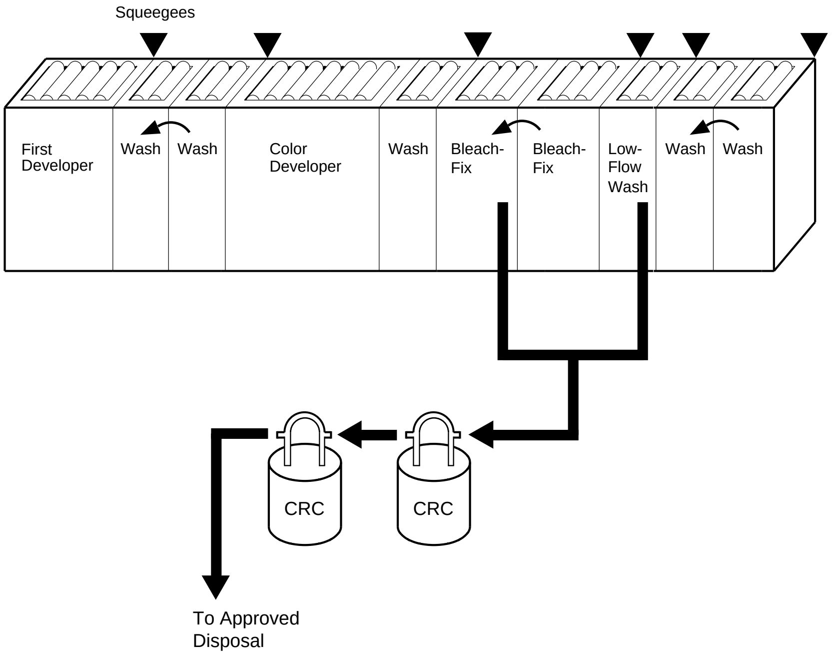

Figure 2

Setup for Silver Recovery with Chemical Recovery Cartridges

WHAT ARE THE CHARACTERISTICS OF CHEMICAL RECOVERY CARTRIDGES?

The KODAK Chemical Recovery Cartridge setup consists of the cartridge and the KODAK Circulating Unit. There are no moving parts or electrical connections. Except for a hose-connection adapter at the processing tank, no special plumbing is required. This simplicity is one of the advantages of chemical recovery cartridges.

You can use chemical recovery cartridges with practically all processing machines and processing methods. All that is required is a controlled flow of silver-bearing solution to the inlet of the recovery cartridge and a suitable drain to discharge the desilvered effluent. You can use these cartridges to recover silver from the combined Process R-3 bleach-fix and low-flow wash overflow, as shown in Figure 2. If your processing volume is high (the processor operates 4 or more hours per day), use two cartridges in series for increased efficiency and as a backup in case the first cartridge fails.

The maximum solution flow rate for the greatest efficiency is 250 mL per minute for a single KODAK Chemical Recovery Cartridge, Model II. The maximum flow rate for two cartridges installed in series is 700 mL / minute. For more information on silver recovery with these cartridges, see KODAK Publication No. J-9, *Silver Recovery with the KODAK Chemical Recovery Cartridge, Model II.*

KODAK CHEMICAL RECOVERY CARTRIDGES

The KODAK Chemical Recovery Cartridge is available in two sizes, the Model II and the Junior Model II. Choose the appropriate cartridge for the volume of solution you will treat. A schematic of the Model II cartridge is shown in Figure 3. KODAK Publication No. J-9 describes the operation and installation for both models of the cartridge.

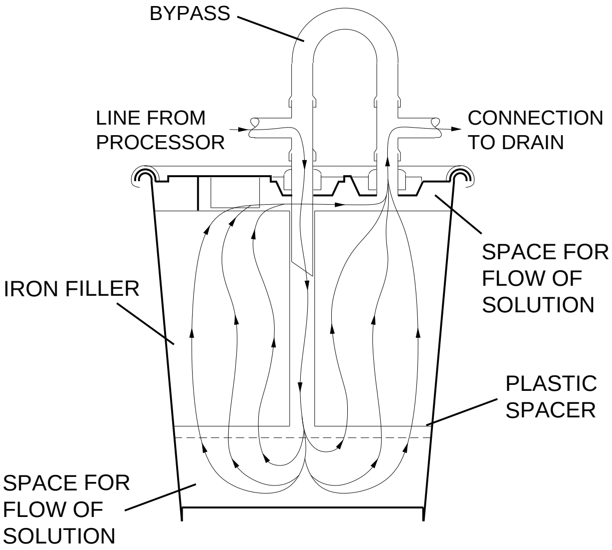

Figure 3

Cross Section of KODAK Chemical Recovery Cartridge

MONITORING THE CARTRIDGES

You can monitor the silver content of the treated effluent with KODAK Silver Estimating Test Papers. These paper strips are impregnated with a chemical that changes color according to the amount of silver present in the solution. By comparing the test papers with the color chart supplied, you can estimate the silver content of the effluent.

To test the effluent from the cartridge, cut a small slit in the top of the plastic drain line near the outlet fitting of the circulating unit. Insert a single test-paper strip into the solution flow for a few seconds. Withdraw the strip and shake off any excess liquid. After about 15 seconds, rinse the test paper briefly with running water and compare the moist strip with the color chart. If the test indicates a concentration of silver greater than 1 g / L, replace the cartridge. Silver estimating test papers are sensitive only to silver concentrations greater than 1 g / L in working-strength solutions.

Test the effluent from each cartridge daily to be sure that the cartridge is functioning properly and that excessive amounts of silver are not being lost in the effluent. Based on the volume of solution processed by the cartridge, make the test daily or more frequently as the cartridge nears exhaustion. After you gain experience with a particular installation, you will be able to judge how often to make the tests.

To avoid the possibility of a misleading test result, always make the test after processing paper for about an hour. This will make sure that the solution you test is typical of that flowing from the cartridge under operating conditions.

Check the Solution Exiting from the Cartridge— Before the bleach-fix enters the cartridge, it is an intense red. Immediately after passing through the cartridge, it is light green or colorless, but contact with the air rapidly makes it red again. The colorless or light green color of the solution at the cartridge exit indicates that the cartridge is operating properly. A rose-colored solution indicates that the cartridge is exhausted and needs to be replaced.

Remember to check the solution color *before* it contacts the air. *Do not* check the color when the processor is stopped; the solution remaining in the circulation tubing will probably already be a light rose color as a result of aerial oxidation.

REPLACING THE EXHAUSTED CARTRIDGE

When the tests indicate that the first cartridge is exhausted, remove it, place the second cartridge in its position, and replace the second cartridge with a fresh one. Transfer a portion of the solution from the exhausted cartridge to the new one. See KODAK Publication No. J-9 or the instructions provided with the cartridge for other information on the installation.

CARTRIDGE PLUGGING

A chemical recovery cartridge may occasionally plug up, causing the solution to flow through the bypass tube of the circulating unit or (in severe cases) to flood the cartridge. First inspect all tubing for kinks; remove the circulating unit and inspect the system for foreign material or crystallization. Has the cartridge been installed properly? Are all plumbing connections properly tightened? You may be able to fix occasional plugging by lifting the cartridge a short distance above its support (about 1 inch) and dropping it to dislodge the blockage.

If plugging is frequent, you can pretreat the solution by reducing the pH before it passes through the cartridges. Figure 4 illustrates the installation of a silver-recovery system with solution pretreatment. This installation requires a storage tank, a preparation tank, two pumps and a flowmeter, and two cartridges for silver removal.

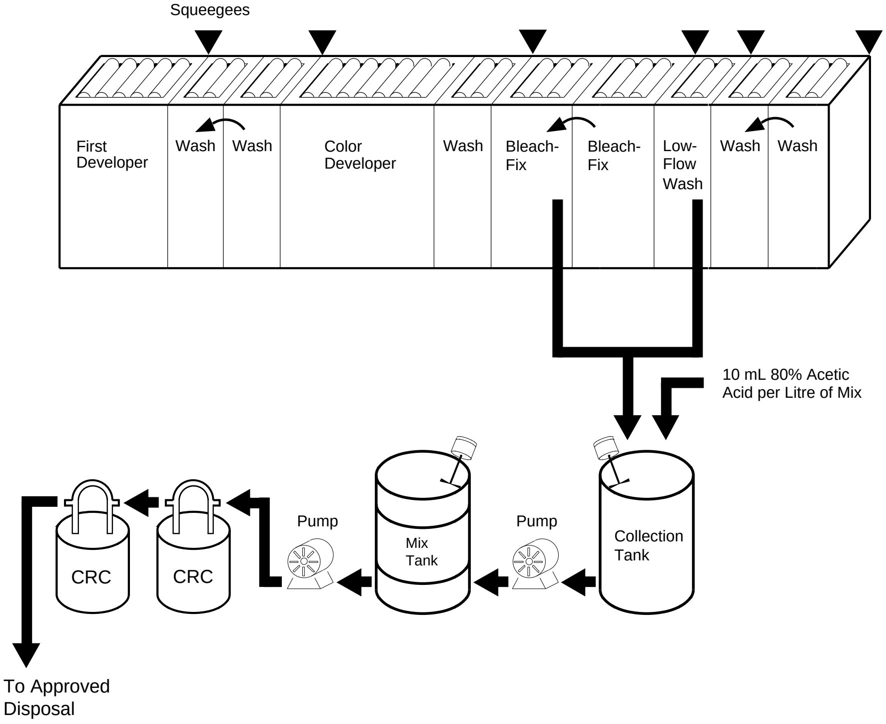

Figure 4

Chemical-Recovery-Cartridge Setup for Pretreatment to Prevent Plugging

***Preparing the solution for silver recovery*—**Collect the overflow from the bleach-fix and the low-flow wash in a storage tank. This tank should have a capacity of about 100 litres and be equipped with a floating cover. Pump the solution into a tank for pretreatment. The pump must be adequate for the distance and the height to which the solution must be pumped. Equip the tank with a stirrer and a means of ventilation. Adjust the pH of the solution to about 5.5 by slowly adding a 50-percent solution of acetic acid while stirring.

Prepare a 50-percent solution of acetic acid by carefully adding glacial acetic acid to cold water in a 1:1 ratio. *Do not* use undiluted glacial acetic acid to adjust the pH; it may cause a precipitate. For a mixture of EKTACHROME R-3 Bleach-Fix and low-flow wash, use about 16 mL of the 50-percent acetic acid solution per litre of the mixture. If you are treating *only* EKTACHROME R-3 Bleach-Fix overflow, use 20 mL of 50-percent acetic acid solution per litre of overflow.

***Silver removal*—**Connect two steel-wool cartridges in series at the exit of the pretreatment tank. The first cartridge completely removes the silver from the solution, and the second serves as a backup if the first cartridge malfunctions. After you adjust the pH, the solution is passed through the cartridges at a constant flow rate by the pump (see Figure 4). At the exit of the second cartridge, test the solution for silver content before discarding it to the sewer.

Figure 5 shows a simple alternate method for labs that do not process continuously, or that want to treat the solution in individual batches. Collect the processor overflow in the pretreatment tank. At the end of a processing run, adjust the pH with acetic acid. Open the tank valve and allow the solution to flow by gravity through the chemical recovery cartridges. The flow rate is controlled by a flow-restricting orifice in the hose between the tank and the first cartridge. The flow rate must not exceed 700 mL/min. Place the tank outlet so that it is slightly higher than the inlet of the first cartridge.

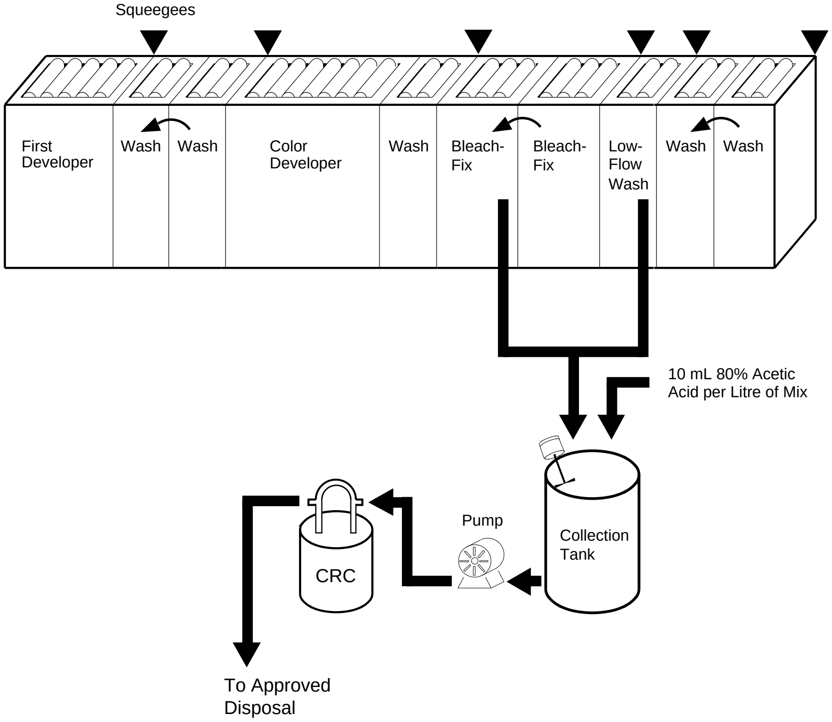

Figure 5

Chemical-Recovery-Cartridge Setup for Pretreatment to Prevent Plugging—Alternate Method

MORE INFORMATION

Kodak has many publications to assist you with information on Kodak products, equipment, and materials.

Complete information on KODAK EKTACHROME RADIANCE III Paper and Select Material is available on the Kodak website **www.kodak.com/go/professional** and through Kodak in your country.

The publications listed below are available from dealers who sell Kodak products, or you can contact Kodak in your country for more information.

J-2A	*Health, Safety, and Environmental Emergency Card*
Y-55	*KODAK Process Record Form*

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Recovering Silver from Processes
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