Using KODAK EKTACOLOR RA Bleach-Fix Regenerator II

By regenerating bleach-fix for Process RA-4, you can reduce the bleach-fix contribution to BOD, COD, and iron in the processing effluent by approximately 40 percent. To regenerate the bleach-fix, collect the overflow, adjust the pH if required, desilver the solution with standard electrolytic recovery methods, and add KODAK EKTACOLOR RA Bleach-Fix Regenerator II.

Note: Depending on your country location, KODAK EKTACOLOR RA Bleach-Fix Regenerator II is available in one of two product versions. Take care to determine which version is available to you. There are different mix ratios for the concentrates when preparing replenisher or fresh tank solutions.

EQUIPMENT AND CHEMICALS

To regenerate your bleach-fix, you will need the following:

- Collection and storage tanks for the bleach-fix and low-flow-wash overflows
- Transfer pumps
- Plumbing to provide separate collection and desilvering of the low-flow wash
- Electrolytic silver-recovery cell capable of desilvering bleach-fixes (see Appendix 1)
- KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Parts A, B, and C
- Means of accurately measuring pH

MODIFYING YOUR PROCESSOR

Use the standard processing steps and conditions for Process RA-4. Note that in Figure 1, the processor is shown with a single bleach-fix tank, you may set up the processor with two tanks. If your processor has more than one bleach-fix tank, plumb the tanks so that the overflow cascades into the preceding tank (countercurrent flow) and the replenisher feeds into the last tank. You'll need to configure the heating and pumping circulation lines to ensure that each tank is treated independently. Tanks cannot be cross-plumbed, which is the case with many processors.

Note: Countercurrent flow is different from the plumbing recommended for processors using KODAK EKTACOLOR RA Bleach-Fix NR. Do **not** use countercurrent flow with a non-regenerated system that uses Bleach-Fix NR; it can cause precipitate to form.

If necessary, install a separate recirculation, filter, and pump system for each bleach-fix tank. Install squeegees between tanks. When the bleach-fix tanks are set up with countercurrent flow, less silver will be lost to the wash.

If you cannot reconfigure the bleach-fix tanks on the processor as described above, it is possible to use KODAK EKTACOLOR RA Bleach-Fix Regenerator II with a single tank. However, you will need to maintain the bleach-fix at a lower pH than in a two-tank system.

You **must** provide for separate collection and desilvering of the low-flow wash. You can desilver the separate low-flow wash electrolytically or with chemical recovery cartridges. Hauling for off-site recovery may also be an option.

If you eliminate the low-flow wash, you will lose considerable silver to the final wash. However, you can recover silver from the final wash by using an ion-exchange method. For more information on the low-flow-wash setup and requirements, see KODAK Publication Nos. J-212, *The Technology of Silver Recovery for Photographic Processing Facilities*, or J-215, *Recovering Silver from Photographic Processing Solutions*.

STARTING UP A REGENERATED BLEACH-FIX SYSTEM

To Prepare a Fresh Working Tank Solution

There are two methods to prepare a fresh working tank solution. The first method uses the EKTACOLOR RA Bleach-Fix Regenerator II concentrates. Mix according to Table 1. Based on the CAT No., note which of the product versions is available in your country and mix according to the ratios in Table 1.

Table 1 Preparing Fresh Tank Solution with KODAK EKTACOLOR RA Bleach-Fix Regenerator II

To Prepare 1 Litre of Fresh Tank Solution		
Start with water	737 mL	716.9 mL
KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part A	CAT No. 105 3131 175.0 mL	CAT No. 525 9452 175.2 mL
KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part B	CAT No. 105 0236 76.0 mL	CAT No. 525 9460 82.0 mL
KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part C	CAT No. 114 6620 12.0 mL	CAT No. 359 7853 25.9 mL
Adjust the pH to 7.0 ± 0.1		

Another method to prepare a fresh bleach-fix tank solution is by diluting KODAK EKTACOLOR RA Bleach-Fix Replenisher NR 1:1 with water. Adjust the pH to 5.5 with 28-percent ammonium hydroxide. (**Tip:** When preparing KODAK EKTACOLOR RA Bleach-Fix Replenisher NR use one half of the amount of Part C, to get the pH close to pH 5.5. Dilute the specially mixed replenisher 1:1 with water for the fresh tank solution).

Note the Cautions for handling acids and bases described in the Appendix 2, page 8.

To Prepare a Fresh Replenisher Solution

There may be times when it will be necessary to prepare a fresh replenisher solution without regenerating existing tank solution. Based on the CAT No., note which version is available in your country and mix according to the ratios in Table 2 that describes the mixing procedure.

Table 2 Preparing Fresh Replenisher Solution with KODAK EKTACOLOR RA Bleach-Fix Regenerator II

To Prepare 1 Litre of Fresh Replenisher Solution		
Start with water	698 mL	698 mL
KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part A	CAT No. 105 3131 210 mL	CAT No. 525 9452 210 mL
KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part B	CAT No. 105 0236 92 mL	CAT No. 525 9460 92 mL
Adjust the pH to 7.0 ± 0.1 with 28% Ammonium Hydroxide		

Bleach-Fix Regeneration

Step 1: Collect the Bleach-Fix Overflow

Install plumbing to collect the overflow from the bleach-fix tank. If you have more than one processor using Process RA-4, you can collect the overflows in a common holding tank. Be sure that the holding tank is large enough to accommodate overflow during peak production periods and during downtime for maintenance and equipment repairs. Equip the collection tank with an overflow port to your lab's secondary silver-recovery system so that you can desilver excess solution before you discard it. Protect the solution from dirt and contamination by using a floating lid and a dust cover on the tank.

Step 2: Desilver the Bleach-Fix Overflow

Depending on processor configuration and the capacity of your silver-recovery cell, you may need to adjust the pH of the bleach-fix overflow to within the range of 7.5 to 8.0 before desilvering.

If the processor has two or more cascaded bleach-fix tanks, it is possible to run the system pH so that the overflow will be close to pH 7.5. At this pH and with a large-capacity silver-recovery cell, no pH adjustment is needed. If you operate a small-capacity silver-recovery system or have a single bleach-fix tank, the tank pH may be slightly low of pH 7.5, adjust the overflow close to pH 7.5 - 8.0 so that the cell and processor capacities will match.

If a pH adjustment is necessary for your system, you can pump the bleach-fix overflow to a mixing tank and adjust the pH there. Or you can pump the overflow to the recovery cell and add the acid or alkali while the solution is recirculating with the desilvering current turned off.

Increase pH by adding 28-percent ammonium hydroxide or 45 % potassium hydroxide. **Do not** use sodium hydroxide to adjust the pH of bleach-fix; it will cause formation of reddish-brown crystals in the solution. Lower the solution pH by adding 20-percent sulfuric acid.

In many operations, the solutions are handled by automated mixing equipment. These machines will mix the amount of acid or alkali into the overflow automatically by adding a predetermined amount of solution.

When the overflow is within the range of pH 7.5 to 8, desilver the solution to a concentration of 1g/L. If you desilver to lower concentrations, poor plate quality will result. The desilvering time and current density will depend on laboratory conditions. Appendix 1 shows how to calculate starting-point conditions. You can adjust these conditions slightly if necessary.

It is important to maintain the pH of the system during desilvering. A pH below 7.5 will reduce the efficiency of the desilvering cell; it will take longer to reduce the silver concentration to 1.0 g/L. If the pH is too high, ammonia vapors will be released.

Step 3: Store the Desilvered Bleach-Fix Overflow

After you have desilvered the bleach-fix overflow, pump it to a storage tank for regeneration as soon as possible. Use a tank suitable for both peak production times and partial downtime. Equip the tank with a floating lid and dust cover.

The regenerator contains chemicals that protect the bleach-fix against oxidation. If you **do not** regenerate the bleach-fix within three days after it is desilvered, add 10 mL of 45-percent potassium sulfite per litre of solution as a preservative.

A regenerated bleach-fix system eventually produces an excess volume of bleach-fix. Therefore, you will need to discard solution at some point. When you need to dispose of surplus volume, you can discharge the desilvered, unregenerated bleach-fix to a terminal silver-recovery system and/or haul it away for disposal.

Step 4: Regenerate the Desilvered Bleach-Fix Overflow

Depending on your country location, use one of the following two mix instructions based on the CAT Nos.

For CAT Nos. 105 3131, 105 0236, and 114 6620

To make 100 gallons of regenerated replenisher, add the full contents of KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Parts A, B, and C, to the volume of overflow specified on the product label (91 gallons [344.5 L]). Stir until the solution is completely mixed.

Table 1a Preparing Bleach-Fix Replenisher from Desilvered Overflow with KODAK EKTACOLOR RA Bleach-Fix Regenerator ll using CAT Nos. 105 3131, 105 0236, and 114 6620

To Prepare 100 Gallons (378.5 Litres)
Start with 91 gallons (344.5 litres) of desilvered bleach-fix overflow
Add 5.12 gallons (1 container) KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part A
Add 3.2 gallons (1 container) KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part B
Add 0.68 gallon (1 bottle) KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part C
Adjust the pH to 7.0 ± 0.1 If you find you need to make consistent adjustments to maintain the pH a nd you consistently have a pH below pH 7 requiring ammonium hydroxide additions, add less Part C. If you consistently have a pH above pH 7 requiring acid addition, increase the amount of Part C

For CAT Nos. 525 9452, 525 9460, and 359 7853

To make 1 litre of regenerated replenisher, add the KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Parts A, B, and C, to the overflow. Stir until the solution is completely mixed.

To Prepare 1 Litre
Start with 904.8 millilitres of desilvered bleach-fix overflow
Add 51.2 millilitres of KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part A, CAT No. 525 9452
Add 32.0 millilitres KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part B, CAT No. 525 9460
Add 12.0 millilitres KODAK EKTACOLOR RA Bleach-Fix Regenerator II, Part C, CAT No. 359 7853
Adjust the pH to 7.0 ± 0.1 If you find you need to make consistent adjustments to maintain the pH and consistently have a pH below pH 7 requiring ammonium hydroxide additions, add less Part C. If you consistently have a pH above pH 7 requiring acid addition, increase the amount of Part C

Measure the pH and adjust it, if necessary, to 7.0 ± 0.1. Add potassium or ammonium hydroxide to increase the pH, or add 20-percent sulfuric acid solution to lower the pH. **Do not** use concentrated sulfuric acid; it will immediately degrade the solution.

When mixing is complete and you have adjusted the pH, transfer the regenerated bleach-fix to the replenisher storage tank.

Monitoring the Bleach-Fix

Bleach-fix regeneration is more complex than many operations in a finishing laboratory. Any error left uncorrected will be compounded in a regenerated system. However, if you mix all solutions correctly, desilver the overflow properly, replenish the processor correctly, and maintain the squeegees in good condition, the system should operate without problems. Maintaining the pH of the system is very important, and requires monitoring as described below.

Monitoring the pH

pH has a significant effect on bleach-fix performance and silver recovery. In some cases, it can also affect cyan dye yield. When the pH in the tank is too low, a condition called “leuco-cyan dye” results in low cyan-dye yield and low red-density plots.

EKTACOLOR RA Bleach-Fix Regenerator II concentrates are designed to maintain the correct pH in a system that has efficient squeegees and is correctly replenished. It also has flexibility to allow adjustments of system pH to accommodate different processor configurations. If squeegee efficiency varies, you will need to control pH by direct pH adjustment or by changing the bleach-fix replenishment rate to maintain the pH.

If the processor has two or more countercurrent plumbed bleach-fix tanks, it is possible to operate at higher pH values. Setting the replenisher at pH 7.0 ± 0.1 will result in an overflow pH of 7.4 to 8.0, depending on processor conditions. At this pH, further adjustment may not be necessary before desilvering.

If the processor has a single bleach-fix tank, the pH of the replenisher and tank solution should be at 7.0 ± 0.1, which will result in an overflow pH of 7.2 to 7.7, depending on processor conditions, squeegee efficiency, and replenishment rate.

If the pH of the overflow does not lie within the specified ranges, check for several possible causes:

- Be sure that the pH meter is operating correctly. It may require recalibration, electrode replacement, or some other repair.
- Check the processor squeegees. Are they worn or out of adjustment?
- Check the bleach-fix replenishment rate. If the pH is low, you may need to reduce the replenishment rate. If the pH is high, you may need to increase the rate.

To raise the pH by 0.5 pH unit, add approximately 15.8 mL of 28% ammonium hydroxide per gallon of overflow. To lower the pH use acetic acid, for instance the KODAK EKTACOLOR RA Bleach-Fix Regenerator, Part C or 20% sulfuric acid.

CONVERTING FROM ANOTHER BLEACH-FIX OR BLEACH-FIX REGENERATOR

To start using EKTACOLOR RA Beach-Fix Regenerator II without dumping existing tank solutions, follow the appropriate procedure below:

To Convert EKTACOLOR RA Bleach-Fix NR to a Regenerated System with EKTACOLOR RA Bleach-Fix Regenerator II

To convert without dumping the seasoned tank solution, prepare a fresh replenisher by diluting KODAK EKTACOLOR RA Bleach-Fix and Replenisher NR 1:1 with water. Adjust the pH to 7.0 with 28% ammonium hydroxide (See Appendix 2 for the preparation of hydroxide and acid solutions for pH adjustment.) Use this solution to replenish your present tank solution.

Desilver and clear the system of any combined bleach-fix and low-flow-wash overflows. Collect the bleach-fix and low-flow-wash overflows separately.

Desilver and regenerate the bleach-fix overflow as described under *Starting Up a Regenerated Bleach-Fix System*. Then replenish with the regenerated solution. During the conversion, adjust the replenishment rate to 247 mL/m^2 (23 mL/ft^2). This will provide a safety factor against retained silver. After a week or two of operation, adjust the rate to 215 mL/m^2 (20 mL/ft^2).

To Convert from EKTACOLOR RA Bleach-Fix Regenerator to EKTACOLOR RA Bleach-Fix Regenerator II

You can use tank solutions, bleach-fix overflow, and replenisher from a regenerated bleach-fix system in a system that uses EKTACOLOR RA Bleach-Fix Regenerator II. At the time of conversion, ensure that any bleach-fix overflow that contains KODAK EKTACOLOR RA Desilvering Concentrate has been desilvered and converted to replenisher. Direct any residual overflow that has not been desilvered to the terminal silver-recovery system. Maintain the replenishment rate at 215 mL/m^2 (20 mL/ft^2).

DIAGNOSING PROBLEMS

Leuco-Cyan Dye

Low bleach-fix pH can cause leuco-cyan dye to form with some papers. Indications of leuco-cyan dye are low red BP, HD–LD, or LD values in the control-strip plot. This type of a problem should be very rare when using KODAK EKTACOLOR EDGE 8 Paper, which is does not form leuco-cyan dye readily.

If you suspect a leuco-cyan dye problem, you can check for it by using a KODAK PROFESSIONAL Pro Strip Color Negative Paper Control Strip / for Process RA-4. Process the control strip as you normally would. After washing and drying, read the density of the BP value. Then dip the control strip in KODAK FLEXICOLOR Bleach III and Replenisher for 2 minutes. Wash and dry the strip, and read the density of the BP value again.

If the increase in the red-density BP value is at least 0.10 more than the increase in the blue and green densities, a leuco-cyan dye problem probably exists. If you verify that leuco-cyan dye is present, check the bleach-fix pH and adjust the bleach-fix replenishment rate as necessary.

Note: Do not use a KODAK Control Strip, Process RA-4, for this test. The strips are manufactured from KODAK EKTACOLOR Edge 8 Paper, which is not subject to leuco-cyan dye problems.

Retained Silver

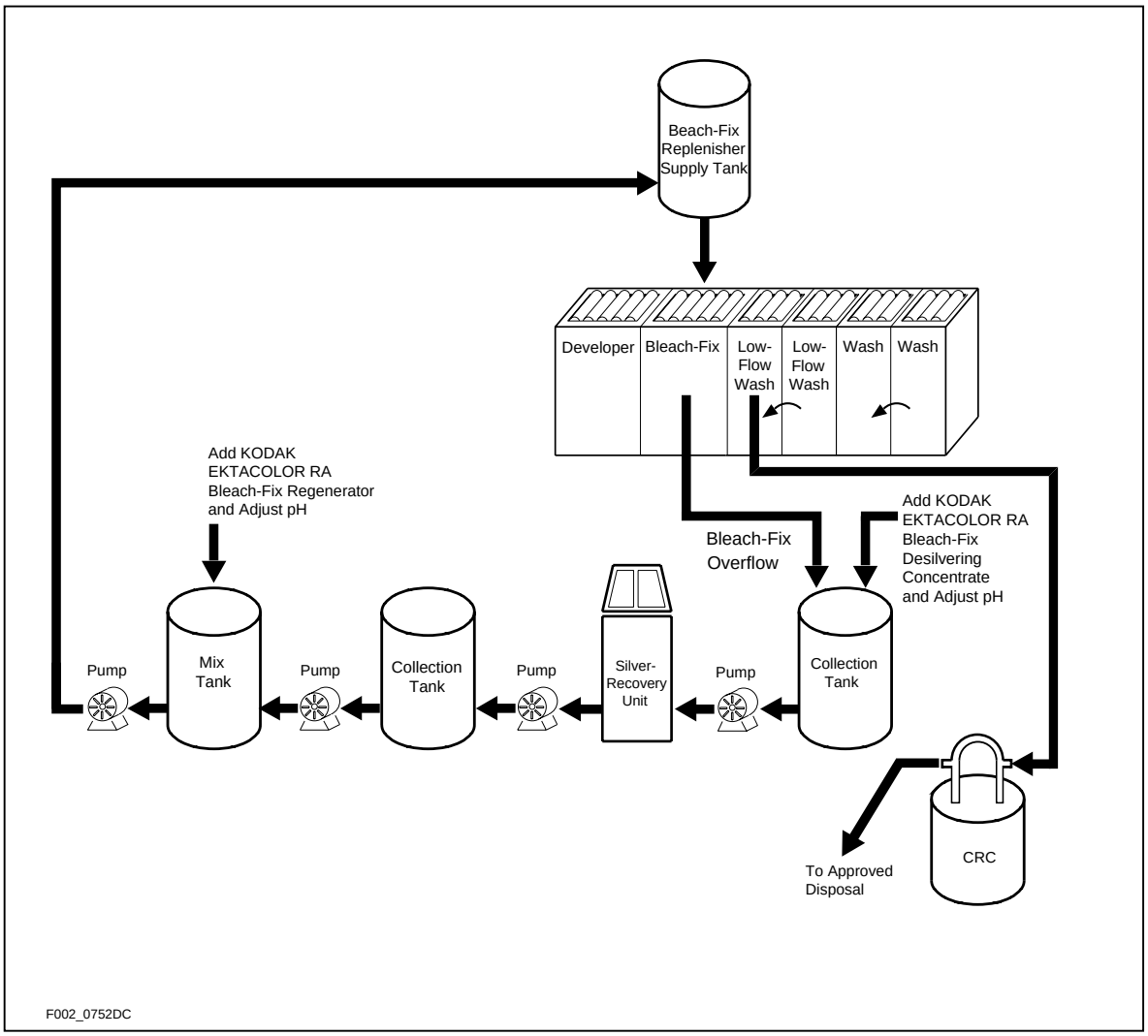
High BP values in the control strip and desaturated colors, especially yellow, in prints are indications of retained silver. You can check for retained silver by visually checking the yellow patch on the control strip, or by viewing the black patch with an infrared viewer. (You can use a KODAK Control Strip, Process RA-4, or a KODAK PROFESSIONAL Pro Strip to check for retained silver.)

Underreplenishment, inefficient squeegees, or high bleach-fix replenisher pH may cause the pH of the tank solution to be too high, and the bleach-fix components to be diluted, which inhibits bleaching. Check that the bleach-fix replenisher meets the specification for your processor configuration. If the replenisher pH is correct and the tank pH is high, the most probable cause is excessive developer carryover.

Configuration for Regenerated Bleach-Fix System

Use the steps and conditions given for Process RA-4; see KODAK Publication No. Z-130, Section 2, *Using KODAK EKTACOLOR Chemicals in Photofinishing Lab*s, or Section 4, *Using KODAK EKTACOLOR RA Chemicals in Professional Finishing Labs*. The bleach-fix replenishment rate for regenerated overflow is 215 mL/m^2 (20 mL/ft^2).

Figure 1 Regenerated Bleach-Fix System



This diagram shows a single bleach-fix tank. If you use two countercurrent tanks, the replenisher is added to the last tank (closest to the wash) and the overflow is collected from the first tank closest to the developer tank.

Appendix 1

Determining Optimum Operating Conditions for Bleach-Fix Regeneration

To determine the optimum operating conditions for your laboratory, you'll need to gather data on lab capacity and needs. It is important to ensure that the capacity of the silver-recovery and regeneration system is significantly larger than the capacity of the processing equipment to generate bleach-fix overflow. This permits future expansion of business and allows for downtime due to equipment failure or scheduled maintenance.

You'll need the following data:

- Desilvering batch size. The physical size of the silver-recovery unit will usually determine batch size.
- Silver concentration in the overflow.
- Silver concentration after desilvering. The aim is approximately 1.0 g/L.
- Cathode surface area. The cathode is the removable electrode from the cell on which the silver plates. Measure the surface area of one side in square metres or square feet.
- Amount of paper processed per day in square metres.
- Theoretical current efficiency of the cell. This data is provided by the equipment supplier.

Bleach-Fix Volume/Batch Size

The volume of bleach-fix generated during a day will be—

Paper processed daily x Replenishment rate in L/m^2

or

m^2 paper per day x 0.215 = Litres of bleach-fix overflow

Most of the overflow is likely to be generated during an 8-hour period of the day, so collection tanks must be adequate to hold at least this volume.

Desilvering will be on a batch basis, and batch size will depend on the capacity of the cell. The desilvering of more than one batch during a 24-hour period may be possible. However, to match the desilvering and regeneration process to the processor capacity, we suggest using a cell that can handle the daily volume of bleach-fix overflow in 15 hours. This will provide flexibility for future expansion and for equipment downtime.

Plating Current

Electrolytically desilver the overflow to approximately 1.0 g/L silver. To obtain good plating, **do not** exceed a current density of 75 amps per square foot (807 amps per square metre) of the cathode area.

For example, if the cathode area is 3 square feet (0.287 square metre), the maximum plating current should not exceed—

75 amps per ft^2 x 3 ft^2 = 225 amps

or

807 amps/ m^2 x 0.287 m^2 = 225 amps

If the plating quality is poor (i.e., if it is very dark or soft, or contains silver sulfide precipitates), decreasing the current may improve plating. If you need more recovery capacity, you may be able to increase plating current by increasing the cathode area. For example, you may be able to install a larger cathode or modify a rotary cathode so that the silver will plate on both sides. See your equipment supplier about possible modifications.

Desilvering Time

Use the following equation to estimate the electrolysis time required to recover silver from a particular batch size. Silver-recovery efficiencies of electrolytic units can vary considerably; use this calculation only as a guide.

$$T = \frac{(S - E) \times V}{A \times 4 \times N}$$

Where:

T = Hours required to desilver a batch of bleach-fix overflow
S = Starting silver concentration in g/L
E = Ending silver concentration in g/L
V = Batch size in litres
A = Amperage per hours through cell
N = Theoretical current efficiency of cell expressed as a decimal (This value is supplied by the manufacturer. If it is not available, a value of 0.2 to 0.25 would be typical.)

Example:
To desilver an 800-litre batch of bleach-fix that has a starting concentration of 4.5 g/L to a final concentration of 1.0 g/L at 165 amps with a current efficiency of 20 percent, the time would be—

$$\text{Time} = \frac{(4.5–1.0) \times 800}{165 \times 4 \times 0.2} = 21.2 \text{ hours}$$

Use KODAK Silver Estimating Test Papers to check the silver concentration. **Do not** try to reduce the silver concentration below 1.0 g/L; it will reduce silver-recovery efficiency and may cause poor plating. No silver is lost by maintaining the silver at 1.0 g/L, because it will be recycled into the bleach-fix replenisher.

Using KODAK EKTACOLOR RA Bleach-Fix Regenerator II

Appendix 2

Preparing Solutions for pH Adjustment

To Prepare 45-Percent Potassium Hydroxide Solution

To prepare one litre of solution, weigh 450 g of potassium hydroxide. Carefully and slowly add it to 1 litre of water in a glass or stainless-steel vessel. Stir until dissolved. Do not use a plastic vessel to dissolve the chemical; considerable heat may be released.

Potassium hydroxide is often commercially available as a nominal 45- to 50-percent solution, which is more convenient.

Note: Ammonium hydroxide is typically available as a nominal 28% solution.

CAUTION: AMMONIUM HYDROXIDE AND POTASSIUM HYDROXIDE ARE STRONGLY CORROSIVE.

Ammonium hydroxide and potassium hydroxide require careful handling; they are strongly corrosive and can cause serious harm to skin and to eyes; they will damage clothing. For your safety, follow these directions for preparing these chemicals for use in pH adjustment. See the Material Safety Data Sheet for handling and precautionary information. Observe *all* CAUTION statements. **Do not** weigh these chemicals in an aluminum container.

To Prepare 20-Percent Sulfuric Acid

Start with four parts cold water. While stirring, slowly add one part concentrated sulfuric acid to the water. **Always** add the acid to the water; **NEVER** add the water to the acid.

Sulfuric acid is often available as more dilute solutions. To minimize handling risk in the lab, you may want to select one of these prepared solutions.

CAUTION: SULFURIC ACID IS CORROSIVE. Sulfuric acid requires careful handling; it is strongly corrosive and can cause serious harm to skin and eyes; it will damage clothing. For your safety, follow these directions for preparing these chemicals for use in pH adjustment. See the Material Safety Data Sheet for handling and precautionary information. Observe *all* CAUTION statements.

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