

6 Processing Options with KODAK EKTACOLOR Chemicals

Process RA-4 is versatile, especially when supported by KODAK EKTACOLOR Chemicals and Kodak expertise. You may be able to obtain additional environmental advantages by using some of the options described in this section:

- Developer regeneration
- Bleach-fix regeneration
- Use of a separate bleach and fixer with regeneration of both solutions
- Using a DRep option instead of bleach and fixer regeneration

REGENERATION AND REUSE OF KODAK EKTACOLOR RA DEVELOPER REPLENISHER 12

KODAK EKTACOLOR RA Developer Replenisher 12 is designed specifically for high-volume processors (i.e., at least one developer-tank turnover per week). To determine tank turnovers, see Section 2, *Using KODAK EKTACOLOR Chemicals in Photofinishing Labs*; Section 3, *Using KODAK EKTACOLOR Chemicals in Minilabs*; or Section 4, *Using KODAK EKTACOLOR Chemicals in Professional Finishing Labs*. You can regenerate EKTACOLOR RA Developer Replenisher 12 overflow with KODAK EKTACOLOR RA Developer Regenerator 12/55. With this regenerator, you do not need to treat the overflow with ion-exchange equipment.

Equipment and Chemicals

Developer regeneration with EKTACOLOR RA Developer Regenerator 12/55 requires very little capital expenditure for equipment. To regenerate developer, you will need the following equipment and chemicals:

- Collection tank for developer overflow
- pH meter that is reliable and accurate
- Buffers and reagents for pH meter adjustment and electrode storage
- KODAK EKTACOLOR RA Developer Regenerator 12/55
- KODAK EKTACOLOR RA Developer Regenerator Converter / RA-4. (Use this product to prepare replenisher solution from KODAK EKTACOLOR RA Developer Regenerator 12/55 when no developer tank overflow is available.)
- Sulfuric acid (20-percent solution) for pH adjustment
- Potassium hydroxide (45-percent solution) for pH adjustment

Regeneration

The regeneration procedure is simple. You collect the overflow, and then add regenerator and water. An important final step is adjusting the pH to compensate for processing conditions and replenishment-rate variations.

A replenisher pH that is too low or too high affects developer activity. Therefore, to maintain consistent developer activity and good process control, you must check the pH of each replenisher mix and adjust it if necessary. KODAK EKTACOLOR RA Developer Regenerator 12/55 requires a minimum amount of acid or base for pH adjustment. This is necessary to compensate for minor differences between labs. It is likely that the amount of adjustment required in a particular lab will be consistent with each regenerated mix.

Be sure that your pH meter is well maintained and calibrated. Without reliable and accurate pH measurements, you will not be able to regenerate the solution properly and maintain developer activity. For information on using, maintaining, and calibrating a pH meter, see *Measuring the pH of Photographic Processing Solutions*. Follow this method carefully to avoid errors in pH adjustment.

If the carryover of developer consistently exceeds 58 mL/m² (5.4 mL/ft²), you will need to add EKTACOLOR RA Developer Replenisher 12 periodically to restore the developer-system volume. To do this, you can keep an inventory of KODAK EKTACOLOR RA Developer Replenisher 12 for regeneration or tank solution losses, or use KODAK EKTACOLOR RA Developer Regenerator Converter / RA-4.

KODAK EKTACOLOR RA Developer Regenerator Converter is designed to be used as an option with a 150-gallon kit of KODAK EKTACOLOR RA Developer Regenerator 12/55 to produce 100 gallons of EKTACOLOR RA Developer Replenisher 12. The converter solution provides the option of eliminating KODAK EKTACOLOR RA Developer Replenisher 12 emergency inventories and carrying costs.

To reduce the effects of oxidation and evaporation, use a floating lid on the storage tank and do not store more developer overflow than you can use within the recommended keeping time.

Use the following procedure to prepare replenisher with EKTACOLOR RA Developer 12 overflow, water, and EKTACOLOR RA Developer Regenerator 12/55:

1. Collect 312 litres (82.5 gallons) of EKTACOLOR RA Developer 12 tank overflow.
2. Add 66.2 litres (17.5 gallons) of water at 21 to 32°C (70 to 90°F).
3. Add the entire contents of Developer Regenerator 12/55 Part A, and stir for 2 minutes.
4. Add the entire contents of Part B, and stir for 2 minutes.
5. Add the entire contents of Part C.
6. Add water at 21 to 32°C (70 to 90°F) to bring the total volume to 568 litres (150 gallons), and stir until the solution is completely mixed.
7. Pass the regenerated replenisher through a filter (similar to that used in the developer recirculation system) when pumping it to the replenisher holding tank to remove any particulates.
8. Check the pH; if it is not within the range of 10.75 to 10.85 at 25°C (77°F), adjust it. Use a 45-percent potassium hydroxide solution to raise the pH; or a 20-percent sulfuric acid solution to lower the pH. Table 6-1 gives starting amounts of these solutions for pH adjustment. You may need to make more than one addition to adjust the replenisher to the correct pH range. For information on how to measure pH, see *Measuring pH*.

The sulfuric acid and potassium hydroxide are available from chemical supply houses.

CAUTION: Potassium hydroxide and sulfuric acid require careful handling; they are strongly corrosive and can cause serious harm to the skin and eyes; they will damage clothing. For your safety, follow the directions below for preparing these chemicals for use in pH adjustment.

- Observe *all* CAUTION statements.
 - Wear appropriate protective clothing and face protection when adding the acid solution to the developer.
 - Add the acid to the developer solution **slowly**; the acid may cause the solution to boil and splash.
 - See the Material Safety Data Sheet and *Safe Handling of Photographic Chemicals* for precautionary and handling information.
9. Record the original pH, the amount of acid or base added, and the final pH. Use this record to monitor additions and to avoid errors. If you get a non-typical pH reading, check the calibration of your pH meter, and retest the pH. For information on checking the pH meter, see *Electrodes*.

Starting Amounts of Potassium Hydroxide and Sulfuric Acid for pH Adjustment

If the pH is *below* 10.75, add 45-percent potassium hydroxide (KOH) in the amounts shown in Table 6-1. If the pH is *above* 10.85, add 20-percent sulfuric acid in the amounts shown in Table 6-1.

Table 6-1

Starting pH	mL 45-Percent Potassium Hydroxide Addition (per 150 gallons)	Starting pH	mL 20-Percent Sulfuric Acid Addition (per 150 gallons)
10.74	174	10.86	264
10.73	200	10.87	306
10.72	230	10.88	350
10.71	260	10.89	394
10.70	288	10.90	438
10.69	316	10.91	482
10.68	345	10.92	526
10.67	373	10.93	570
10.66	402	10.94	614
10.65	432	10.95	658
10.64	460	10.96	702
10.63	489	10.97	746
10.62	518	10.98	790
10.61	546	10.99	834
10.60	576	11.00	876
10.59	604		
10.58	632		
10.57	662		
10.56	690		
10.55	718		
10.54	747		
10.53	776		
10.52	806		
10.51	834		
10.50	862		

Preparing the Sulfuric Acid Solution

To prepare a 20-percent (7.2 N) solution of sulfuric acid, start with 4 parts of cold water. Stir the water, and *slowly* add 1 part concentrated (36 N) sulfuric acid. Twenty-percent sulfuric acid is also available from some vendors; however **do not** use 20-percent *fuming* sulfuric acid (40 N), because it is super-concentrated, very hazardous to handle, and more expensive. **Always** add the acid to the water; **never** add the water to the acid.

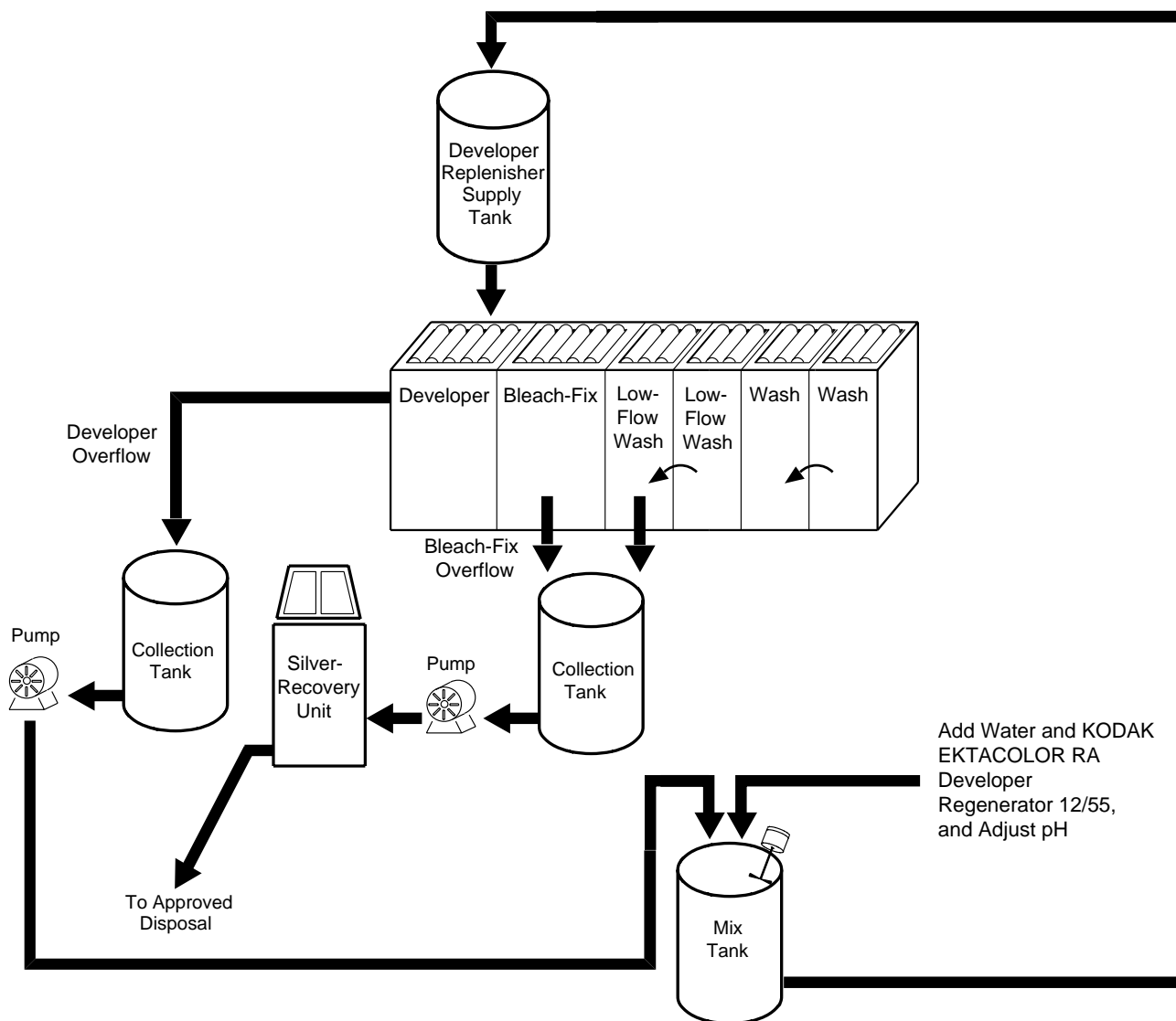
CAUTION: SULFURIC ACID IS CORROSIVE. Sulfuric acid requires careful handling; it is strongly corrosive and can cause serious harm to the skin and eyes; it will damage clothing. For your safety, follow these directions for preparing these chemicals for use in pH adjustment. See the Material Safety Data Sheet for handling and precautionary information. Observe *all* CAUTION statements. Avoid contact with skin or clothing by solution. Always use appropriate protective equipment including: gloves, goggles, and aprons to protect your eyes and skin. For more information, see *Safe Handling of Photographic Chemicals*.

Processing Conditions

Use the steps and conditions given for Process RA-4 (see Section 2, *Using KODAK EKTACOLOR Chemicals in Photofinishing Labs*, or Section 4, *Using KODAK EKTACOLOR Chemicals in Professional Finishing Labs*).

The replenishment rate for replenisher prepared from regenerated overflow is 129 mL/m² (12 mL/ft²), the same as for EKTACOLOR RA Developer Replenisher 12.

Figure 6-1



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REGENERATING KODAK EKTACOLOR RA BLEACH-FIX

By regenerating Process RA-4 bleach-fix, you can reduce the bleach-fix contribution to the BOD, COD, and iron in the processing effluent by approximately 40 percent. To regenerate Process RA-4 bleach-fix, collect the overflow, treat it with KODAK EKTACOLOR RA Bleach-Fix Desilvering Concentrate, electrolytically desilver it, and add KODAK EKTACOLOR RA Bleach-Fix Regenerator.

Equipment and Chemicals

To start regenerating your bleach-fix, you will need the following equipment and chemicals:

- Collection and storage tanks for the bleach-fix and the low-flow-wash overflows
- Transfer pumps
- Electrolytic silver-recovery cell (capable of desilvering bleach-fixes, with sufficient capacity)
- Plumbing to provide separate collection and desilvering of the low-flow wash water (**do not** eliminate the low-flow wash unless you plan to recover silver from the final wash by using ion-exchange methods; too much silver may be lost)
- KODAK EKTACOLOR RA Desilvering Concentrate
- KODAK EKTACOLOR RA Bleach-Fix Regenerator

Changing Your Processor

Use the standard processing steps and conditions for Process RA-4. If your processor has more than one bleach-fix tank, plumb it so that the overflow cascades into the preceding tank (countercurrent flow) and the replenisher enters the last tank. This is different from the plumbing recommended for use with EKTACOLOR RA Bleach-Fix Replenisher NR. You **must not** use countercurrent flow with a non-regenerated system that uses bleach-fix NR; it may cause a precipitate to form.

Install a separate recirculation, filter, and pump system for each tank. Install squeegees between tanks. When your processor is set up with a countercurrent-flow bleach-fix, less silver is lost to the wash.

You **must** also provide for separate collection and desilvering of the low-flow wash. You can desilver the separate low-flow wash water electrolytically or with chemical recovery cartridges. If you eliminate the low-flow wash, you will lose too much silver in the final wash. However, if you eliminate the low-flow wash, you can recover silver from the final wash by using an ion-exchange method. For more information on low-flow wash setup and requirements, see KODAK Publication No. J-212, *The Technology of Silver Recovery for Photographic Processing Facilities*.

Getting Started

There are two ways to begin regenerating Process RA-4 bleach-fix. Your choice will depend on your current process and the needs of your lab. You can—

- Start regeneration with a fresh bleach-fix
- Convert to a regenerated system from EKTACOLOR RA Bleach-Fix NR without dumping the current bleach-fix

To Start Fresh

To begin a regenerated system with a fresh bleach-fix, dump your present bleach-fix tank solution and replenisher. Prepare a fresh bleach-fix by diluting KODAK EKTACOLOR RA Bleach-Fix and Replenisher NR 1:1 with water. Adjust the pH to 5.5 with ammonium hydroxide. Use this mix as tank solution and replenisher.

Note: Although this is the easiest method for starting a regenerated bleach-fix system, it costs more, and discarding the old solutions is a greater burden on the sewage treatment system. If these are concerns, consider converting the current bleach-fix.

To Convert a Process RA-4 Bleach-Fix NR to a Regenerated System

To convert an existing non-regenerated bleach-fix to a regenerated system 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 5.5 with ammonium hydroxide. Use this solution to replenish your present tank solution. Desilver and clear the collection tank of any combined bleach-fix and low-flow-wash overflows. Collect the bleach-fix and low-flow-wash overflows separately.

Bleach-Fix Replenishment—Adjust the bleach-fix replenishment rate to 247 mL/m² (23 mL/ft²) to start; this provides a safety factor against retained silver. After a week or two of operation, adjust this rate to 215 mL/m² (20 mL/ft²).

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 overflow from each in a common holding tank. Be sure that the holding tank is large enough to store overflow during peak production periods, maintenance, and equipment malfunctions. Equip the tank with an overflow port with a plumbing connection to your laboratory's secondary silver-recovery system so that you can desilver the 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

This step includes treatment with EKTACOLOR RA Desilvering Concentrate and electrolytic desilvering.

KODAK EKTACOLOR RA Desilvering Concentrate—

Before desilvering the overflow, add EKTACOLOR RA Desilvering Concentrate. The desilvering concentrate adjusts the pH of the overflow for more efficient silver recovery and provides some of the chemicals necessary for regeneration.

Start with an amount of bleach-fix overflow shown in Table 6-2 and add the corresponding amount of EKTACOLOR RA Desilvering Concentrate.

IMPORTANT: You **must** add the correct amount of desilvering concentrate. Adding too little or too much will cause problems, such as leuco-cyan dye, retained silver, and formation of iron precipitates in the bleach-fix (see *Diagnosing Problems*).

You can pump the bleach-fix overflow to a mixing tank and add the concentrate, or pump the overflow to the recovery cell and add the concentrate when the power is off and while the batch is recirculating. The recirculation should provide adequate mixing.

After you add the desilvering concentrate, check the pH to be sure that it is within a range of 7.5 to 8.0. A low pH reduces silver-recovery efficiency; a high pH causes ammonia vapor to be released. If the pH is not within this range, raise it by adding ammonium hydroxide or lower it by adding sulfuric acid. See *Fixer* for instructions on preparing and handling sulfuric acid.

Note: Remember that it is very important to add the correct amount of KODAK EKTACOLOR RA Desilvering Concentrate to obtain the right chemical balance in the replenisher. Mixing the wrong amount of concentrate or overflow will cause bleach-fix problems. **Do not** use the concentrate to increase the bleach-fix pH; use ammonium hydroxide.

Table 6-2 Preparing the Bleach-Fix Overflow for Desilvering with KODAK EKTACOLOR RA Desilvering Concentrate

To Prepare 1 Litre	To Prepare 100 U.S. Gallons
Start with 950 mL bleach-fix overflow.	Start with 95 gal bleach-fix overflow.
Add 50 mL KODAK EKTACOLOR RA Desilvering Concentrate.	Add 1 unit KODAK EKTACOLOR RA Desilvering Concentrate.
Adjust pH if necessary to 7.5 to 8.0; increase with ammonium hydroxide or decrease with dilute sulfuric acid.	
Electrolytically desilver this mixture to a silver concentration of 1 g/L.	

Electrolytic Desilvering—Electrolytically desilver the overflow to approximately 1 g/L of silver. To obtain good plating, **do not** exceed a current density of 75 amps/square foot (807 amps/square metre) of cathode area. For example, if the cathode area is 3 square feet (0.287 square metres), the maximum plating current should not exceed

$$75 \text{ amps/ft}^2 \times 3 \text{ ft}^2 = 225 \text{ amps}$$

or

$$807 \text{ amps/m}^2 \times 0.287 \text{ m}^2 = 225 \text{ amps}$$

If the plating quality is poor (i.e., if it is dark or crumbly, 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 (install a larger cathode or modify a rotary cathode so that silver will plate on both sides). See your equipment supplier about possible modifications.

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 as a guide only.

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

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 recovery cell expressed as a decimal

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:

$$\text{Time} = \frac{(4.5 - 1.0) \times 800}{165 \times 4 \times 0.20} = 21.2 \text{ hours}$$

Use silver-estimating test papers to check the silver concentration. **Do not** try to reduce the silver concentration to less than 1 g/L; it will reduce recovery efficiency and may cause poor plating. No silver is lost by maintaining the concentration at 1 g/L, because it will be recycled in the bleach-fix replenisher (see Figure 6-2).

Step 3: Store the Desilvered Bleach-Fix Overflow

After you have desilvered the bleach-fix overflow, pump it to a storage tank. Use a tank size suitable for both peak production and potential downtime. Equip the tank with a floating lid and a dust cover. Since a regenerated bleach-fix system eventually produces excess solution, you will need to discard solution at some point. Equip the tank with an overflow that has a plumbing connection to your lab's secondary silver-recovery system so that you can desilver the excess solution before you discard it.

Note: We recommend that you add the regenerator (see *Step 4: Regenerate the Desilvered Bleach-Fix Overflow*) as soon as possible after desilvering; 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.

Step 4: Regenerate the Desilvered Bleach-Fix Overflow

Take the amount of desilvered overflow shown in Table 6-3 and add the corresponding amounts of EKTACOLOR RA Bleach-Fix Regenerator, Part A and Part B. Stir until the solution is completely mixed. Measure the pH and adjust it, if necessary, to 5.50 ± 0.10 . Add ammonium hydroxide to increase the pH or a 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. Install a filter in the transfer line between the mixing tank and the replenisher tank to filter out any dirt or precipitates.

Table 6-3 Preparing Bleach-Fix Replenisher from Desilvered Bleach-Fix Overflow and KODAK EKTACOLOR RA Bleach-Fix Regenerator

To Make 1 Litre	To Make 110 U.S. Gallons
Start with 892 mL desilvered bleach-fix overflow.	Start with 98 gal desilvered bleach-fix overflow.
Add 34.2 mL KODAK EKTACOLOR RA Bleach-Fix Regenerator, Part A.	Add 1 unit KODAK EKTACOLOR RA Bleach-Fix Regenerator, Part A.
Add 73.8 mL KODAK EKTACOLOR RA Bleach-Fix Regenerator, Part B.	Add 2 units KODAK EKTACOLOR RA Bleach-Fix Regenerator, Part B.
Adjust pH if necessary to 5.5 ± 0.1 . Increase with ammonium hydroxide or decrease with dilute sulfuric acid.	

CAUTION: AMMONIUM HYDROXIDE IS CORROSIVE. Ammonium hydroxide requires careful handling; it is strongly corrosive and can cause serious harm to the skin and eyes; it will damage clothing. See the Material Safety Data Sheet for handling and precautionary information. Observe *all* CAUTION statements. Avoid contact with skin or clothing by solution or vapors. Use a ventilation hood to avoid exposure to vapors. **Do not** weigh hydroxides in an aluminum container.

To Prepare a 20-Percent Solution of Sulfuric Acid

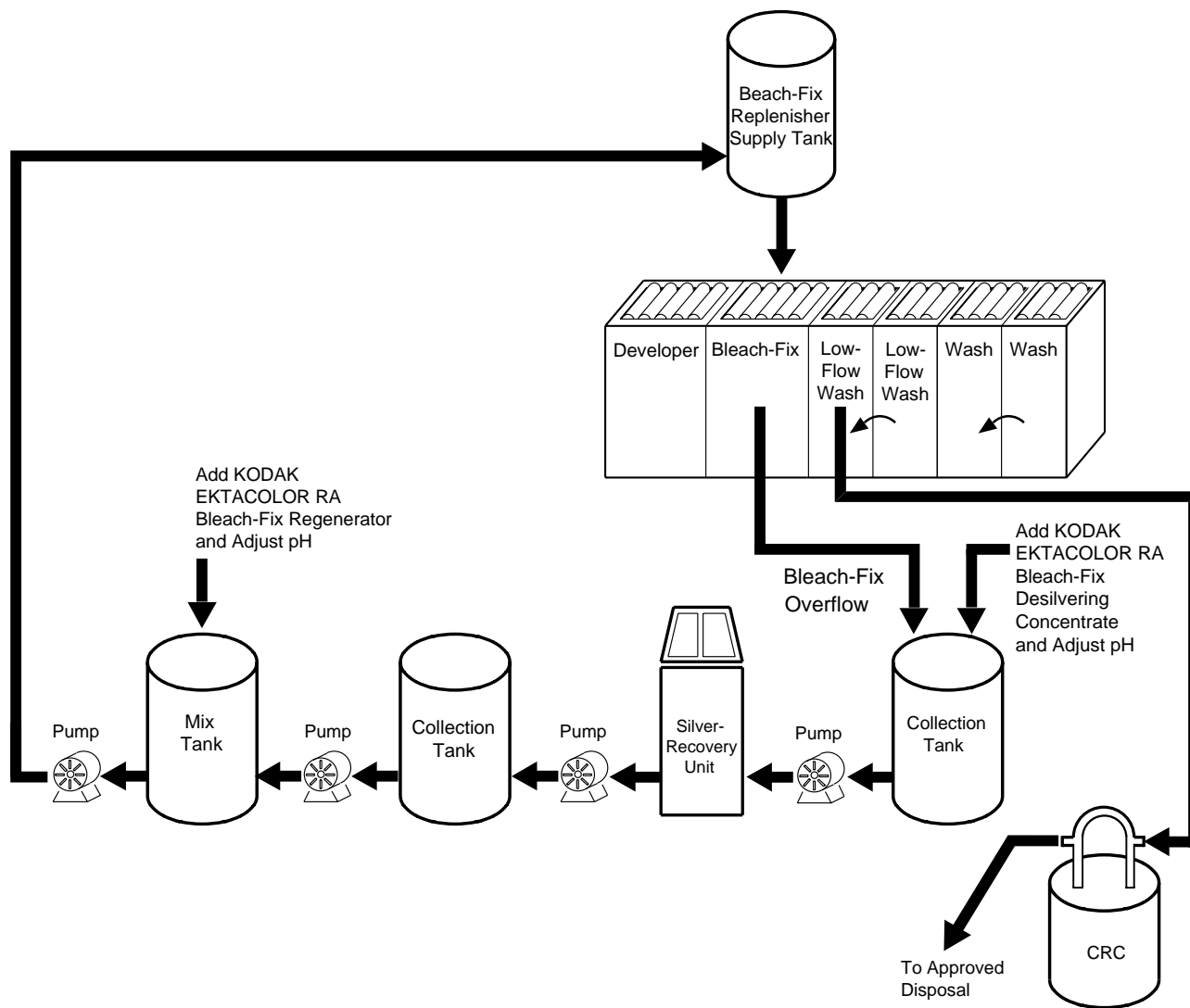
Start with 4 parts cold water. While stirring, *slowly* add 1 part concentrated sulfuric acid to the water. **Always** add the acid to the water; **never** add the water to the acid.

CAUTION: SULFURIC ACID IS CORROSIVE. Sulfuric acid requires careful handling; it is strongly corrosive and can cause serious harm to the skin and eyes; it will damage clothing. See the Material Safety Data Sheet for handling and precautionary information. Observe *all* CAUTION statements. Avoid contact with skin or clothing by solution. Always use appropriate protective equipment including: gloves, goggles, and aprons to protect your eyes and skin. For more information, see *Safe Handling of Photographic Chemicals*.

Processing Conditions

Use the steps and conditions given for Process RA-4; see Section 2, *Using KODAK EKTACOLOR Chemicals in Photofinishing Labs*, or Section 4, *Using KODAK EKTACOLOR Chemicals in Professional Finishing Labs*. The bleach-fix replenishment rate for regenerated overflow is 215 mL/m² (20 mL/ft²).

Figure 6-2



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Monitoring the Bleach-Fix

Bleach-fix regeneration is more complex than most operations in a finishing lab. Any error left uncorrected is compounded in a regenerated system. However, if you mix all solutions correctly, add the correct amount of desilvering concentrate, desilver the overflow properly, replenish correctly, maintain the squeegees well, and carefully monitor and adjust the pH, the system should operate without problems.

Monitor the pH—pH has the greatest effect on bleaching, silver recovery, and leuco-cyan dye formation. The regenerator concentrate is balanced to maintain the correct pH in a system that has efficient squeegees and that uses the correct replenishment rate. If squeegee efficiency varies, you will need to adjust the replenishment rate to maintain the pH of the bleach-fix.

The aim pH for bleach-fix replenisher and fresh tank solution is 5.50 ± 0.10 . The pH of the seasoned tank solution and overflow will be 6.00 to 6.50. Adding the desilvering concentrate increases the pH of the bleach-fix overflow to 7.5 to 8.0. The pH of the desilvered overflow will vary. After you add KODAK EKTACOLOR RA Bleach-Fix Regenerator, the pH of the replenisher should be 5.50 ± 0.10 .

If the pH of the bleach-fix is not within 5.40 to 5.60, check these possible causes:

- First check to see that the pH meter is operating properly. It may require recalibration, electrode replacement, or some other repair. For information on checking your pH meter and the electrodes, see *Electrodes*.
- Check the squeegees. Are they worn or out of adjustment?
- Check the bleach-fix replenishment rate. Remember that the required rate depends on the efficiency of the squeegees. If the pH is low, you may need to *reduce* the replenishment rate; if the pH is high, you may need to *increase* the replenishment rate. After regeneration, check the pH of the replenisher to determine if it is correct.

To monitor your bleach-fix system, keep a record of the pH of the bleach-fix during each stage of regeneration—the collected overflow, the overflow with the desilvering concentrate, the regenerated solution, and the pH-adjusted solution. For information on how to measure pH, see *Measuring the pH of Photographic Processing Solutions*.

Diagnosing Problems

Leuco-Cyan Dye—T

Note: The recently introduced KODAK EKTACOLOR Edge 8 Paper, ROYAL VIII Paper, and KODAK DURALIFE Paper are insensitive to leuco-cyan dye. With these papers, leuco-cyan dye will not form at low pH values. Other papers will be sensitive to this problem, including KODAK Pro Strips, Process RA-4.

In Process RA-4, bleach-fix regeneration problems rarely occur. However, 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 density values in the control-strip plot. If you suspect a leuco-cyan-dye problem, you can check for it by dipping the control strip in KODAK

FLEXICOLOR Bleach III and Replenisher for 2 minutes, and then washing and drying it. (For details of the test, see *Rebleaching Test for Leuco-Cyan Dye*). If the red BP density value increases by at least 0.10 more than the green and blue density values, there is probably a leuco-cyan-dye problem. If you verify that leuco-cyan dye is present, check the bleach-fix pH and adjust the bleach-fix replenishment rate as necessary.

Retained Silver—High BP density values in the control strip and desaturated colors in the prints are indications of a retained-silver problem. You can check for retained silver by visually checking the yellow patch on the control strip or viewing the BP patch on the control strip with an infrared scope. Retained silver is usually caused by too high a pH or dilution of the bleach-fix tank solution. A seasoned bleach-fix tank solution should have a pH of 6.00 to 6.50.

Underreplenishment, inefficient squeegees, or high replenisher pH may increase the pH of the bleach-fix tank solution. Check that the bleach-fix replenisher pH is 5.50 ± 0.10 . If the replenisher pH is correct, the most probable causes are excessive developer carried over into the bleach-fix tank or a bleach-fix replenishment rate that is too low. Check the condition of the squeegees before adjusting the replenishment rate.

Precipitates—Precipitates in the bleach-fix have three possible causes: incorrect mixing of the desilvering concentrate, sodium compounds in the bleach-fix system, and overconcentration of a developer compound in the bleach-fix.

A *reddish-brown sludge* indicates improper mixing of KODAK EKTACOLOR RA Desilvering Concentrate with the bleach-fix overflow. An incorrect mix ratio causes iron oxide to form.

Reddish-brown crystals are most often caused by using sodium compounds for pH adjustment (sodium hydroxide) or as a preservative (sodium sulfite). Correct the problem by switching to ammonium or potassium compounds.

A *purple precipitate* indicates that too much of a particular developer component is carried over into the bleach-fix. If this occurs, check and adjust the squeegee between the developer and the bleach-fix to reduce developer carryover into the bleach-fix. Also check the temperature of the bleach-fix tank solution. Change the recirculation filters in the processor and the silver-recovery cell more often than normal until the problem is corrected.

USING SEPARATE BLEACH AND FIXER SOLUTIONS

A primary advantage of using a separate bleach and fixer for Process RA-4 is the reduced discharge of BOD, COD, iron, ammonia, sulfates, chelates, and solids. KODAK EKTACOLOR RA Bleach Regenerator and KODAK EKTACOLOR RA Fixer Regenerator use no ammonia salts and are especially useful in meeting stringent ammonia discharge restrictions. Silver recovery is also more efficient. However, using a separate bleach and fixer requires a larger processing machine and more attention to some aspects of process control.

To determine whether this option will meet your needs, contact your Kodak sales representative. Note that the recommendations given in this section apply *only* to processes using Kodak chemicals and papers; they may not yield satisfactory results with other manufacturer's products.

Equipment and Chemicals

You will need the following equipment and chemicals in addition to those you are currently using:

- Additional processor tanks (depending on the processor)
- Two replenisher tanks
- Plumbing for processor tanks and replenisher and wash lines
- Two collection tanks
- Plumbing to provide separate collection and desilvering of the low-flow wash water. Use a low-flow wash for maximum silver recovery unless you plan to recover silver from the final wash by using an ion-exchange method.
- Two to four pumps
- Electrolytic silver-recovery cell (capable of desilvering fixers, with sufficient capacity)
- Glacial acetic acid
- KODAK EKTACOLOR RA Bleach Regenerator
- KODAK EKTACOLOR RA Fixer Regenerator
- pH meter

Getting Started

Your processor must be designed or modified for the separate bleach and fixer option. Install sufficient replenisher and processor tanks to set up your processor like the diagram in Figure 6-3.

If your processor now uses Process RA-4 with a bleach-fix, you will need to install additional processor, replenisher, and holding tanks, plumbing, and pumps. Dump the bleach-fix by discharging it in small amounts in an acceptable manner; check with your local sewer-code authority.

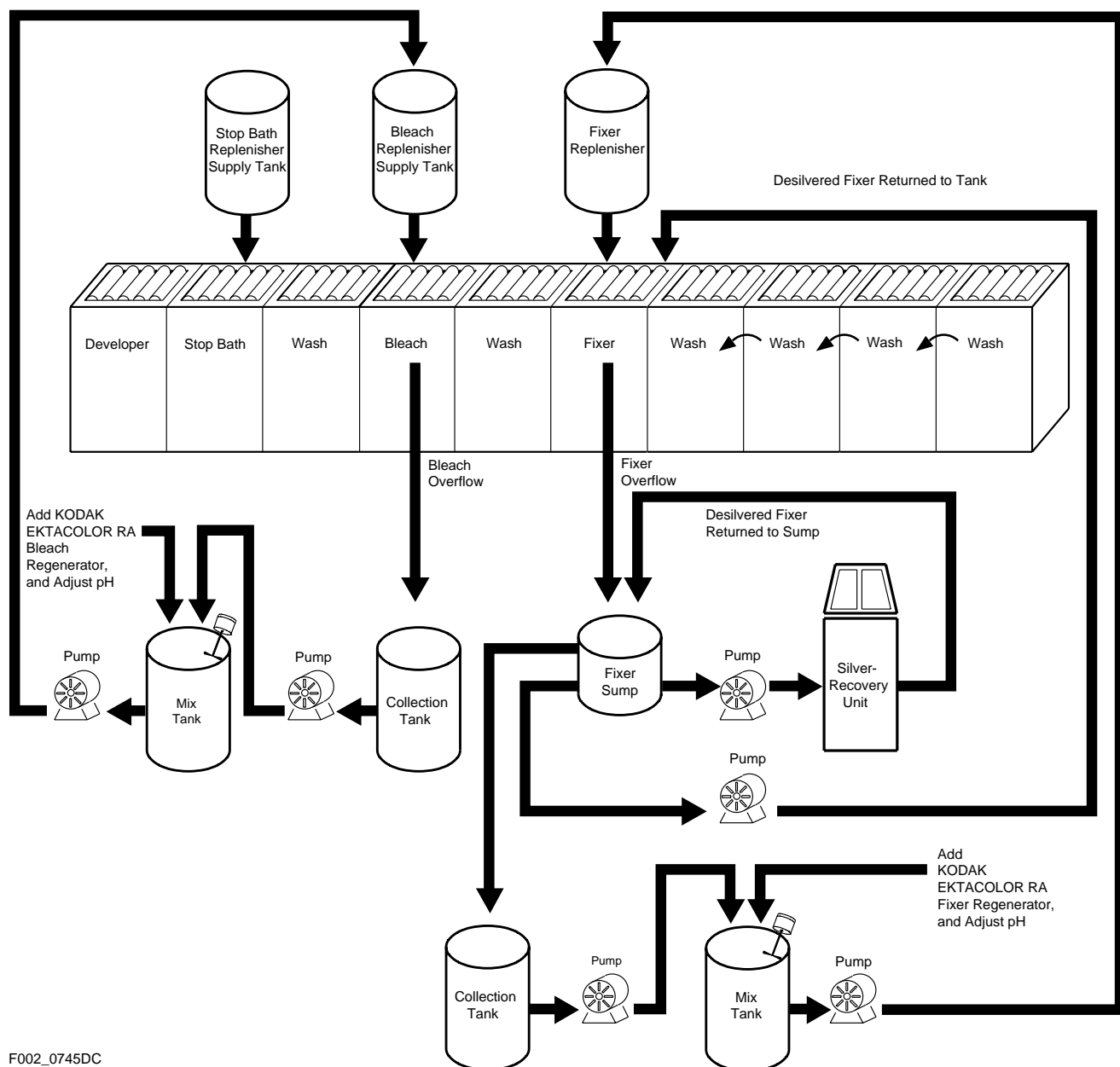
Prepare a bleach tank solution and a bleach replenisher solution from KODAK EKTACOLOR RA Bleach Regenerator (or from replenisher prepared from regenerator) according to the directions packaged with the chemicals. Prepare a fixer tank solution and replenisher from KODAK EKTACOLOR RA Fixer Regenerator.

Install a stop bath and a wash or an acid rinse. To use a stop bath, your processor **must** have at least two tanks available to install a stop bath and a wash before the bleach tank. If only one tank is available, install an acid rinse. Formulas for these solutions are given in *Preparing the Solutions*.

Processing Sequence

The processing sequence with a separate bleach and fixer is developer, stop bath, wash, bleach, wash, fixer, and final wash (see Figure 6-3). The stop bath is necessary to stop development and to minimize the amount of developer carried into the bleach. The wash following the stop bath reduces the possibility of stain by removing developing agents from the paper to minimize carryover into the bleach. If your processor does not have enough tanks for a stop bath and a wash, you may be able to use a single acid-rinse tank instead (see *Acid Rinse*).

Figure 6-3 Separate Bleach and Fixer Option



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Preparing the Solutions

Whether you use a stop bath and a wash or an acid rinse, you will need to prepare a stop bath and replenisher. If your processor is set up with a stop bath and a wash, use the stop-bath formula to prepare replenisher and tank solution. If your processor uses the acid-rinse option, prepare the acid-rinse tank solution by mixing the stop bath and water.

Stop Bath

To use a stop bath, your processor must have at least two tanks for the stop bath and a wash before the bleach tank. Install efficient squeegees at the exit of each tank. Use the replenishment rates given in Table 6-14 as starting points. If a range is given, use the midpoint of the range for your replenishment rate. If your processor has only one tank available, use the acid-rinse option.

Maintain the pH of the stop bath at 4.70 ± 0.25 . If the pH is too *high*, a magenta stain may occur. To lower the pH, *increase* the replenishment rate of the stop bath. If the pH of the stop bath is too *low* for an extended period, the carryover can lower the pH of the bleach to an unacceptable level. To increase the pH, *decrease* the replenishment rate of the stop bath. If you change the stop-bath replenishment rate, make a proportional change in the stop wash rate also.

Table 6-4 Preparing Stop Bath and Replenisher

To Make 1 Litre
Start with 900 mL water (at room temperature).
Add 7 mL glacial acetic acid (stir for 1 minute).
Add water to make 1 litre.
Stir for 5 minutes.
The aim pH is 4.70 ± 0.25 for a seasoned tank. The pH of a fresh tank will be approximately 3.00 to 3.50.

Acid Rinse

If you do not have enough processor tanks to use a separate stop bath and a wash, you can combine the functions into a single acid rinse. Using an acid rinse gives less protection against stain, but it is a suitable alternative if you properly maintain the squeegees and replenishment rates. If staining occurs, you may also need to increase the acetic acid by increasing the amount of stop bath. The acid rinse uses the same stop-bath formula and the same replenishment rates as the stop bath and wash, but the two are combined in a single tank.

To replenish the acid rinse, meter the stop bath and the water separately. Begin replenishing with the stop-bath solution at 215 mL/m^2 (20 mL/ft^2) and the water at 2150 mL/m^2 (200 mL/ft^2). The aim pH for the acid rinse is 4.70 ± 0.25 . Adjust the rate of the stop bath or water to maintain the aim pH; the rate will vary depending on the amount of developer carryover. When you set the replenishment rate, adjust the stop-wash-water flow rate proportionately and maintain a sufficient flow for adequate washing. After you have had more experience with the process, you can increase the concentration of acid in the stop bath and use a lower replenishment rate. Using a higher concentration of acid lets you mix the stop-bath solution for the rinse less frequently. For example, if you double the concentration of the stop bath, you can reduce the replenishment rate of the stop bath by 50 percent and maintain the tank-solution pH of 4.70 ± 0.25 .

If the pH is too *high*, a magenta stain may occur. To correct the problem, lower the pH by increasing the replenishment rate of the stop bath and stop-wash water. If the pH of the acid rinse is too *low*, increase the pH by reducing the replenishment rate of the stop bath. For information on how to measure pH, see *Measuring the pH of Photographic Processing Solutions*.

Table 6-5 Preparing an Acid-Rinse Tank Solution

To Make 1 Litre
Start with 900 mL water.
Add 100 mL stop bath and replenisher.
The aim pH is 4.70 ± 0.25 for a seasoned tank. The pH of a fresh tank will be approximately 3.00 to 3.50.

Bleach

Use Table 6-6 to prepare a fresh replenisher from KODAK EKTACOLOR RA Bleach Regenerator concentrate and water. (You will need this replenisher at startup until you collect enough bleach overflow to regenerate.) Use Table 6-7 to prepare replenisher from bleach overflow and regenerator. This is the replenisher formula that you will routinely use as you regenerate the bleach. You can prepare tank solution directly from the regenerator (Table 6-8) or from the replenisher (Table 6-9).

After mixing the bleach, test and adjust the pH to 5.00 ± 0.10 by using ammonium hydroxide or dilute sulfuric acid. The specific gravity of the tank solution should be 1.036 ± 0.003 at 27°C (80°F). Replenisher specific gravity should be 1.055 at 27°C (80°F).

CAUTION: AMMONIUM HYDROXIDE AND SULFURIC ACID ARE CORROSIVE. Avoid contact with skin or clothing by solution or vapors. Use a ventilation hood to avoid exposure to vapors. **Do not** weigh these chemicals in an aluminum container. See the Material Safety Data Sheet for precautionary and handling information. Always use appropriate protective equipment including: gloves, goggles, and aprons to protect your eyes and skin. For more information, see *Safe Handling of Photographic Chemicals*.

Use a bleach replenishment rate of 129 mL/m^2 (12 mL/ft^2). The pH of the bleach tank solution should be 5.00 ± 0.25 ; the pH of the replenisher should be 5.00 ± 0.10 . A high pH can cause staining. For information on how to measure pH, see *Measuring the pH of Photographic Processing Solutions*.

Do not use metal cleaners that contain phosphate to clean bleach tanks or other processing or mixing equipment; phosphate from any source can severely contaminate the bleach and lead to precipitates.

Table 6-6 Preparing Bleach Replenisher from KODAK EKTACOLOR RA Bleach Regenerator and Water

To Make 1 Litre	To Make 60 Gallons
Start with 600 mL water (at room temperature).	Start with 40 gal water (at room temperature).
Add 250 mL bleach regenerator concentrate.	Add 15 gal bleach regenerator concentrate.
Add water to make 1 litre.	Add water to make 60 gallons.
Bleach replenisher specific gravity: 1.056 ± 0.003 at 25°C (77°F) 1.054 ± 0.003 at 30°C (86°F) 1.052 ± 0.003 at 35°C (95°F)	
The aim pH is 5.00 ± 0.10 (increase with ammonium hydroxide or decrease with dilute sulfuric acid).	

Table 6-7 Preparing Bleach Replenisher from Bleach Overflow and KODAK EKTACOLOR RA Bleach Regenerator

To Make 1 Litre	To Make 150 Gallons
Start with 901 mL bleach overflow.	Start with 135 gal bleach overflow.
Add 99 mL bleach regenerator concentrate.	Add 15 gal bleach regenerator concentrate (1 drum).
Bleach replenisher specific gravity: 1.056 ± 0.003 at 25°C (77°F) 1.054 ± 0.003 at 30°C (86°F) 1.052 ± 0.003 at 35°C (95°F)	
The aim pH is 5.00 ± 0.10 (increase with ammonium hydroxide or decrease with dilute sulfuric acid).	

Table 6-8 Preparing Bleach Tank Solution from KODAK EKTACOLOR RA Bleach Regenerator and Water

To Make 1 Litre
Start with 700 mL water.
Add 165 mL bleach regenerator concentrate.
Add water to make 1 litre.
Bleach tank solution specific gravity: 1.037 ± 0.003 at 25°C (77°F) 1.035 ± 0.003 at 30°C (86°F) 1.033 ± 0.003 at 35°C (95°F)
The aim pH is 5.00 ± 0.25 (increase with ammonium hydroxide or decrease with dilute sulfuric acid).

Table 6-9 Preparing Bleach Tank Solution from Bleach Replenisher and Water

To Make 1 Litre
Start with 240 mL water.
Add 660 mL bleach replenisher.
Add water to make 1 litre.
Bleach tank solution specific gravity: 1.037 ± 0.003 at 25°C (77°F) 1.035 ± 0.003 at 30°C (86°F) 1.033 ± 0.003 at 35°C (95°F)
The aim pH is 5.00 ± 0.25 (increase with ammonium hydroxide or decrease with dilute sulfuric acid).

Fixer

Use Table 6-10 to prepare replenisher from KODAK EKTACOLOR RA Fixer Regenerator concentrate and water. Use Table 6-11 to prepare replenisher from fixer overflow and regenerator. The starting fixer replenishment rate is 64.8 mL/m² (6 mL/ft²). To use this rate in an in-line desilvering system, you **must** maintain the tank-solution silver concentration in the range of 0.5 to 2.0 g/L. If you **do not** use in-line desilvering, increase the replenishment rate.

Prepare fixer tank solution by mixing KODAK EKTACOLOR RA Fixer Regenerator and water (Table 6-12) or fixer replenisher and water (Table 6-13).

Note: KODAK EKTACOLOR RA Fixer Regenerator is formulated with no ammonium salts and causes no ammonia discharge. For this reason, you should use sodium hydroxide to adjust the pH rather than ammonium hydroxide.

Table 6-10 Preparing Fixer Replenisher from KODAK EKTACOLOR RA Fixer Regenerator and Water

To Make 1 Litre	To Make 90 Gallons
Start with 600 mL water.	Start with 50 gal water.
Add 333 mL fixer regenerator concentrate.	Add 30 gal fixer regenerator concentrate (1 drum).
Add water to make 1 litre.	Add water to make 90 gal.
The aim pH is 7.5 (decrease with dilute sulfuric acid). You will need approximately 7.5 mL/L of 20% solution of sulfuric acid (7N) to adjust for the substantially higher pH of the regenerator.	

Table 6-11 Preparing Fixer Replenisher from Fixer Overflow and KODAK EKTACOLOR RA Fixer Regenerator

To Make 1 Litre	To Make 150 Gallons
Start with 800 mL fixer overflow.	Start with 120 gal fixer overflow.
Add 200 mL fixer regenerator concentrate.	Add 30 gal fixer regenerator concentrate (1 drum).
Fixer replenisher specific gravity made from seasoned-tank overflow: 1.093 ± 0.005 at 25°C (77°F) 1.091 ± 0.005 at 30°C (86°F) 1.089 ± 0.005 at 35°C (95°F)	
The aim pH is 7.5 (increase with sodium hydroxide or decrease with dilute sulfuric acid).	

Table 6-12 Preparing Fixer Tank Solution from KODAK EKTACOLOR RA Fixer Regenerator and Water

To Make 1 Litre
Start with 800 mL water.
Add 167 mL fixer regenerator concentrate.
Add water to make 1 litre.
Fixer seasoned tank solution specific gravity: 1.050 ± 0.003 at 25°C (77°F) 1.048 ± 0.003 at 30°C (86°F) 1.046 ± 0.003 at 35°C (95°F)
The aim pH is 7.5. You will need approximately 3.5 mL/L of 20% solution of sulfuric acid (7N) to adjust the pH. The pH of a seasoned tank with in-line desilvering is 6.0 to 7.0.

Table 6-13 Preparing Fixer Tank Solution from Fixer Replenisher and Water

To Make 1 Litre
Start with 500 mL replenisher.
Add water to make 1 litre.
Fixer seasoned tank solution specific gravity: 1.050 ± 0.003 at 25°C (77°F) 1.048 ± 0.003 at 30°C (86°F) 1.046 ± 0.003 at 35°C (95°F)
The aim pH is 7.5 (increase with sodium hydroxide or decrease with dilute sulfuric acid). The pH of a seasoned tank with in-line desilvering is 6.0 to 7.0.

CAUTION: SODIUM HYDROXIDE AND SULFURIC ACID ARE CORROSIVE. Avoid contact with skin or clothing by solution or vapors. Use a ventilation hood to avoid exposure to vapors. **Do not** weigh these chemicals in an aluminum container. See the Material Safety Data Sheet for precautionary and handling information. Always use appropriate protective equipment including: gloves, goggles, and aprons to protect your eyes and skin. For more information, see *Safe Handling of Photographic Chemicals*.

To Prepare a 20-Percent Solution of Sulfuric Acid

Start with 4 parts cold water. While stirring, *slowly* add 1 part concentrated sulfuric acid to the water. **Always** add the acid to the water; **never** add the water to the acid.

Processing Conditions

Table 6-14 Processing Steps and Conditions—Separate Bleach and Fixer Option for Process RA-4

Solution/Step	Time* min:sec	Temperature °C (°F)	Replenishment Rate mL/m ² (mL/ft ²)†	Comments
EKTACOLOR RA Developer Replenisher 12 or EKTACOLOR RA Developer Replenisher	0:45	37.8 ± 0.3 (100.0 ± 0.5) 35 ± 0.3 (95 ± 0.5)	129 (12) 161 (15)	Recirculate and filter. Use squeegees at tank exit.
Stop Bath‡	0:30	29 to 35 (85 to 95)	108 to 323 (10 to 30)	Recirculate and filter. Use squeegees at tank exit.
and Wash or Acid Rinse§	0:30 0:30	29 to 35 (85 to 95)	1080 to 3230 (100 to 300)	Use squeegees at tank exit.
	0:30	29 to 35 (85 to 95)	Stop-bath solution: 108 to 323 (10 to 30) Water: 1080 to 3230 (100 to 300)	The acid rinse replaces the stop bath <i>and</i> wash if that option is used. Recirculate and filter. Use squeegees at tank exit.
Bleach	1:30	29 to 35 (85 to 95)	129 (12)¶	Recirculate and filter. Use squeegees at tank exit.
Wash	0:45	29 to 35 (85 to 95)	2150 (200)	Use squeegees at tank exit.
Fixer	0:45	29 to 35 (85 to 95)	65 (6)**	Recirculate and filter. Use squeegees at tank exit.
Wash	1:30	29 to 35 (85 to 95)	See wash rates for Process RA-4††	Use squeegees at tank exit.

* Immersion time plus crossover time to the next tank. For best results, use the recommended times with a crossover time of 6 seconds or less.

† These rates are for KODAK EKTACOLOR Edge 8 and PROFESSIONAL SUPRA III Papers and KODAK PROFESSIONAL DURAFLEX Print Material. For rates for other papers and materials, see Section 4, *Using KODAK EKTACOLOR Chemicals in Professional Finishing Labs*.

‡ Materials used in the stop-bath replenishment system should be suitable for use with acetic acid (some materials suitable for other acids are not suitable for use with acetic acid). To avoid premature pump failure and reduce costs, control replenishment with flowmeters and solenoid valves rather than precision metering pumps.

§ Replenish the acid rinse with stop bath diluted 1:9 with water. Add the acid and water to the suction side of the recirculation pump; this provides adequate mixing of the replenisher and tank solutions. Recirculate at 0.20 to 0.35 tank turnovers per minute. Adjust the replenishment rates to provide adequate flow to neutralize developer carryover and to maintain pH of the tank solution.

¶ Assumes use of efficient squeegees. You may need to adjust the replenishment rate depending on stop-bath (or acid-rinse) carryover.

** This fixer replenishment rate is intended to maintain a silver concentration of 0.5 to 2.0 g/L in the tank solution in an in-line desilvering system. If the silver concentration is higher, you may need to increase the replenishment rate.

†† See Section 2, *Using KODAK EKTACOLOR Chemicals in Photofinishing Labs*, or Section 4, *Using KODAK EKTACOLOR Chemicals in Professional Finishing Labs*.

Diagnosing Problems

With the separate bleach and fixer option, increased staining can result from excessive amounts of developing agents carried into the bleach over an extended period. Other symptoms of excessive developer carryover include—

- Bleach pH frequently higher than the aim
- Tar or black particles suspended in the bleach solution
- Silver retention in the paper
- Leuco-cyan dye (in some papers and materials)

These problems occur because the bleach is made less active by excessive developer carry-in. Using a stop bath and a wash instead of an acid rinse gives increased protection against these problems.

If staining occurs:

- Check the squeegees after the developer, stop bath, and wash; poorly functioning squeegees may be the cause of the problem.
- Check the pH of the stop bath or acid rinse. If the pH is above aim, increase the replenishment rate of the stop bath.
- Check the flow rate of the wash after the stop bath; it should be proportional to the stop-bath rate (100 mL of wash water for every 10 mL of stop bath).
- Check the pH of the bleach; high pH may be a cause of the stain. Although correcting the bleach pH may reduce staining, it will not eliminate the cause—excessive amounts of developing agents carried into the bleach.

Once you correct the cause, it may take several days of processing to season out the developing agents.

If you cannot maintain staining at an acceptable level or if staining is a recurring problem, try the following steps. If you process KODAK PORTRA III, SUPRA III, or ULTRA III Papers, use this method as a standard practice.

1. Reduce the pH of the stop bath or acid rinse to 4.0 to 4.5 by increasing the stop-bath replenishment rate or by increasing the concentration of the acetic acid in the stop bath. This will decrease developer carry-in and increase the amount of acetic acid consumed.
2. Add 2 g/L of sodium metabisulfite to the stop bath. This decreases the amount of stain formed by developer carry-in.
3. Replace the filters in the bleach recirculation line with charcoal filters. You can use these filters occasionally, as needed, or continuously to remove the developing agents. These filters will eliminate the cause of the stain very quickly; however, they will require frequent changing, especially if there is a lot of stain.

DREP OPTION FOR KODAK EKTACOLOR RA BLEACH REGENERATOR AND KODAK EKTACOLOR RA FIXER REGENERATOR

If your processor is set up to use a separate bleach and fixer, you can reduce labor and save space by using the DRep option. Using this option eliminates mixing and regeneration, and the space needed for those operations. It also reduces the space needed for chemical and replenisher storage. Effluent discharge levels should not be affected.

Instead of the usual routine of regenerating the bleach and fixer (collecting overflow, regenerating, adjusting pH, and transferring the treated solution to replenisher storage), simply feed the regenerator concentrates directly into the processor tanks *at very low rates*. You eliminate all the other steps, including pH adjustment.

With the DRep option, you should check the pH and specific gravity of the bleach and fixer tank solutions, and monitor squeegee wear frequently to maintain an in-control process.

Equipment and Chemicals

To convert, you need storage tanks of the proper size for the concentrate, and you must equip the processor with pumps capable of delivering small volumes of replenisher. Then adjust the bleach and fixer replenishment rates. These modifications are relatively simple.

You don't need to change any of the solutions; this option uses the same chemicals used for separate bleach and fixer, but in concentrated form. Flush the lines and prime them with the chemical concentrates.

You will need the following equipment:

- Two replenisher storage tanks (high-density polypropylene or Type 316 stainless steel) of a size that will hold a 2- to 4-week supply of bleach or fixer concentrate.
- Two pumps that can accurately and precisely meter out small volumes of replenisher concentrate (pump and valve seals should be made of EPDM).
- $\frac{3}{4}$ -inch (20 mm) hard PVC piping, reinforced PVC, or Teflon hose for replenisher lines from the tanks to the processor.

Because the replenisher is used in concentrated form, you don't need a replenisher storage tank as large as those needed for standard bleach and fixer replenishment. The tanks should hold approximately a 2- to 4-week supply of bleach and fixer concentrate. You can eliminate bleach and fixer overflow storage tanks and some solution-transfer stations. If the replenishers supply multiple processors, install junctions in the lines.

To prevent chemical spills, install a solenoid valve in the replenisher line near the replenisher supply tanks. Connect the solenoid valve to the replenisher pump relay so that the concentrates flow only during replenishment.

You can also replenish directly from the drums of concentrate. If you do, provide a signal to indicate when the drum is empty, a way to change drums and transfer residual concentrate, and a way to bleed air from the replenisher lines.

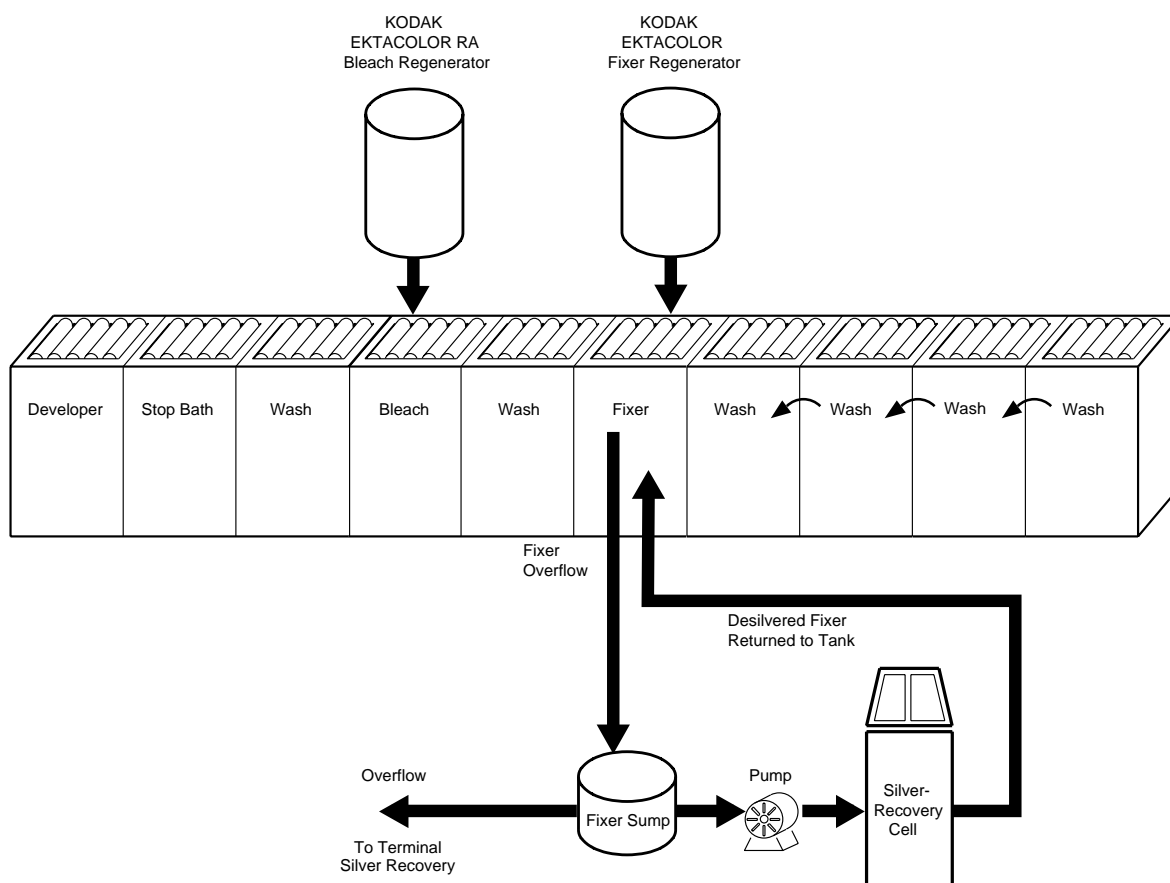
Processing Conditions

Use the processing conditions given in Table 6-14 for Process RA-4 with a separate bleach and fixer, except the bleach and fixer replenishment rates. You must adjust the bleach and fixer replenishment to the lower rates for the DRep option. A simple calibration or adjustment should be all that is needed. If smaller pumps are needed, several inexpensive precision pumps are available; ask your Kodak sales representative. At a carryover rate of about 65 mL/m² (6 mL/ft²), the starting replenishment rates are—

Solution	mL/m ²	mL/ft ²
Bleach	12.9	1.2
Fixer	12.9	1.2

If solution carryover is greater, increase replenishment rates to compensate. Check the replenishment rates frequently for the first two weeks after converting to be sure that the system is operating properly. Use the same silver-recovery method that you used for in-line silver recovery from the fixer with standard replenishment.

Figure 6-4



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MEASURING THE pH OF PHOTOGRAPHIC PROCESSING SOLUTIONS

Correct pH is important in photographic processing, because the solutions **must** remain within a specified pH range to produce good results. To use any of the options in this section you **must** be able to make accurate pH readings.*

The pH Scale

pH is a measurement of the acidity or alkalinity of a substance. There are hundreds of acids—strong acids like sulfuric acid, which can dissolve steel nails—and weak acids like boric acid, which is safe enough to use as an eyewash. There are also many alkaline solutions, called “bases”—mild alkaline solutions that soothe upset stomachs—and strong alkaline solutions such as lye and sodium hydroxide, which dissolve human hair.

Acids and bases have a characteristic that lets us tell them apart and that we can measure—the concentration of hydrogen ions. Strong acids have high concentrations of hydrogen ions; weak acids have low concentrations. pH then is a numerical value that expresses the hydrogen ion concentration.

The real numerical values for these hydrogen ion concentrations are typically a very small fraction (1/10,000,000, for example). Because that’s an inconvenient number to work with, a unique scale was devised. The scale created uses the negative logarithm of the hydrogen ion concentration (or activity) for acidic and basic solutions. Values read from this scale are called “pH” measurements.

Numbers from 0 to 7 on the scale indicate acid solutions; 7 to 14 indicate alkaline solutions. The more acidic a substance is, the closer its pH will be to 0; the more alkaline a substance, the closer its pH will be to 14. Some photographic solutions are neither highly acidic or highly alkaline but are closer to the neutral point, pH 7—the pH of tap water. Developer solutions measure on the alkaline portion of the pH scale, typically ranging from pH 9 to 12. Stop baths measure on the opposite end of the scale because they contain large amounts of acid; they typically have pH values of 1 to 3.

How Is pH Measured?

A simple way to determine whether a material is an acid or base is to use litmus paper. Litmus paper is a treated paper strip that turns pink when dipped in an acid solution and blue when dipped into an alkaline solution. Although other pH papers can now provide a more accurate pH estimate, they are not accurate enough for measuring photographic solutions and they are not very useful for measuring the pH of colored or turbid liquids.

The most accurate and commonly used method for measuring pH is using a pH meter and a pair of electrodes. A pH meter is basically a very sensitive voltmeter. The electrodes connected to it will generate an electrical current when they are immersed in solutions.

Two types of electrodes are used to measure pH, and each electrode has a specific purpose. The “glass” electrode has a bulb made of special composition glass that is very selective and sensitive to hydrogen ions. When this glass bulb is immersed in a solution, the voltage generated at the bulb’s surface is related to the pH of the solution.

The other electrode is called the “reference electrode.” It provides a stable and reproducible voltage when it is immersed in a solution. When the two electrodes are connected to a pH meter, the voltage difference is amplified and displayed on an analog or digital meter. An electrode that combines both the pH-sensitive glass bulb and a reference cell in one electrode body is called a “combination electrode”; it is used in the same way as an electrode pair. For accuracy and consistency, you **must** standardize the meter with solutions with known pH values called “buffers.” A buffer is a specially prepared solution with two important qualities: it resists changes in pH, and it has a specific pH value at a specific temperature.

For accurate and reliable pH readings, you **must** maintain and calibrate the pH meter and the electrodes often. You **must** also measure the solutions at the correct temperature and use the proper technique.

The pH Meter

The pH meter **must** be capable of two-point calibrations with an adjustable slope control or a readout of slope values. Readability to 0.01 pH unit and accuracy to ± 0.02 are required.

The Corning 450 pH meter, or equivalent, is a satisfactory single-channel meter. This meter accommodates one pair of electrodes. However, you can upgrade it with accessories to accommodate multiple pairs of electrodes. The Orion EA 940 pH meter, or equivalent, is a satisfactory dual-channel meter. Two pairs of electrodes can be attached simultaneously.

* For a more detailed description of the pH test method that includes buffer calibration methods, you can purchase a copy of publication ANSI/NAPM IT4.36-1995 (or current revision) from American National Standards Institute, 11 West 42nd Street, New York, NY 10036.

Electrodes

For increased accuracy, use a separate pair of electrodes or at least a separate “glass” electrode for high and low pH measurements. Store electrodes in the recommended solutions. Rinse and fill reference electrodes with 3.5 M rather than saturated potassium chloride solution. The lower salt concentration produces less crystallization inside the electrodes and in the reference junction. The complex composition of photoprocessing solutions can produce unwanted effects on the glass membranes of pH electrodes. Use the following reference and glass electrodes to avoid pH differences that occur with reference elements and the pH-sensitive glass of some manufacturers.

Although electrodes that combine reference and glass electrodes in a single probe can perform satisfactorily, it is easier to maintain and troubleshoot a reference and glass pH electrode pair.

Recommended Reference Electrodes

- Corning 476002, reference, ceramic junction, calomel
- Corning 476360 (formerly 476171), reference, reverse sleeve

Recommended Glass pH Electrode

- Corning 476024, glass, rugged bulb US Standard Connector

Buffers and Reagents

Buffers can change with age or storage conditions. See the manufacturer’s literature for the expiration dates of individual solutions. When possible, store the buffers in their original container. Replace the buffers used for meter calibration at least once each 8-hour shift or work day; replace them more often with frequent use. Change the buffers if you have difficulty calibrating the meter.

Calibrating Buffers

Buffer	Manufacturer/Catalog Number
pH 4.00 ± 0.01 at 25°C (77°F)	Fisher SB101-20* VWR Cat 34180-639 or equivalent
pH 7.00 ± 0.01 at 25°C (77°F)	Fisher SB107-20* VWR Cat 34180-661 or equivalent
pH 10.00 ± 0.02 at 25°C (77°F)	Fisher SB115-20* or equivalent

* 20-litre collapsible plastic cube.

Reagents

Reference-Electrode Filling Solution (3.5 M Potassium Chloride)

Purchase 4 M (saturated) potassium chloride from a manufacturer below (or equivalent).

Reagent	Manufacturer/Catalog Number
Reference Electrode Filling Solution, 4 M KCl	Beckman 566468
Internal Filling Solution, 4 M KCl	Orion 900014
Saturated KCl	Corning 477000

To prepare a 3.5 M potassium chloride solution, add 87.5 mL of 4 M (saturated) potassium chloride (KCl) solution to a 100 mL volumetric flask. Add distilled water to bring the solution to 100 mL. This solution is stable for 6 months.

Electrode Storage Buffer

(0.1 M Potassium Chloride in pH 7 Buffer)

Add 2.5 mL of 4 M (saturated) potassium chloride solution to a 100 mL volumetric flask. Add pH 7 calibrating buffer to bring the solution to 100 mL. This solution is stable for 6 months.

Glass-Electrode Storage Buffer

Use the pH 7 electrode storage buffer (described above) to store glass pH electrodes.

Temperature

Careful control of temperature is essential for precise and accurate measurement of pH. A change in temperature of 1°C (2°F) produces a change of 0.015 to 0.020 pH unit in measurements of carbonate-buffered developers of about pH 10. Use a water bath with circulation around the sample containers to equilibrate all samples and buffer solutions. Maintain the sample and buffer temperature at 25 ± 0.25°C (77 ± 0.5°F) for 15 minutes before making the measurement.

Stirring

For greatest precision, stir solutions during meter calibration and sample pH measurement. Stir the sample moderately during measurement so that the electrodes are exposed to a uniform sample. Avoid vigorous stirring that draws a large amount of air into the solution; it can oxidize the solution. Use air-, water-, or electrically-driven magnetic stirrers that can be immersed in the water baths.

Measuring pH

Use the following method* to measure the pH of photographic processing solutions. You can use wide-mouthed jars with caps (8-ounce size) to hold buffers and sample solutions. Cover the sample solutions and buffers while bringing them to equilibrium temperature to reduce aerial oxidation and evaporation, and to prevent contamination and accidental dilution.

1. Bring the fresh buffers and the solutions you are measuring to a stable temperature of 25°C (77°F). For solutions of pH 7 to 14, use pH 7 and 10 buffers (for high-range pH meter calibration). For solutions of pH 0 to 7, use pH 4 and 7 buffers (for low-range pH meter calibration). For more information on buffers, see *Buffers and Reagents*.
2. Change the reference-electrode fill solution as described in *Reference Electrode—Care/Rejuvenation*, and attach the electrodes to the meter.
3. Set the pH meter temperature compensator to 25°C (77°F). Adjust the manual control to this value, or if the meter is controlled by a microprocessor, input the value through the keypad. See the meter instruction manual for specific instructions on meter calibration.
4. Calibrate the pH meter at both the high and the low range.

High-Range pH Meter Calibration

5. Rinse the electrodes with distilled or demineralized water; blot excess water from the tips of the electrodes (and any protective assemblies) with a soft tissue. *Do not* rub the electrode membrane with the tissue; hold the tissue near the electrode surface and allow it to draw off the water.
6. Immerse the electrodes in pH 7 calibrating buffer stirred with a Teflon-coated stirring bar and magnetic stirrer, or a paddle-type stirrer rinsed with distilled or demineralized water.
7. Wait 2 minutes for the electrodes to reach equilibrium and for the meter reading to stabilize. If after this time the meter does not display the pH value given by the manufacturer for the pH 7 calibrating buffer at 25°C (77°F), set the *calibration* control to the correct value.

8. Rinse the electrodes with distilled or demineralized water, blot them, and immerse them in pH 10 calibrating buffer (stirred as before).
9. Wait 2 minutes for the electrodes to reach equilibrium and for the meter reading to stabilize. If after this time the meter does not display the pH value given by the manufacturer for the pH 10 calibrating buffer at 25°C (77°F), set the *slope* control to the correct value.
10. Repeat steps 5 through 9 until the meter displays the pH values of the calibrating buffers (± 0.005 pH units).
11. Read the slope value. If it is not within 98 to 102 percent of optimum electrode response, repeat steps 5 to 9. If the slope is still out of range, try another glass electrode.

Low-Range pH Meter Calibration

12. Repeat steps 5 to 11, but substitute the pH 4 buffer for the pH 10 buffer.

Sample pH Measurement

13. Bring the sample to a stable temperature of 25°C (77°F). A sample of 80 to 120 mL is adequate. You can use an 8-ounce (approximately 250 mL) wide-mouth jar as a sample container.
14. Calibrate the meter for the required pH range and temperature of the sample. Verify that the sample temperature is $25 \pm 0.25^\circ\text{C}$ ($77 \pm 0.5^\circ\text{F}$).
15. Rinse the electrodes with distilled or demineralized water, blot them, and immerse them in the sample as it is stirred.
16. Wait 2 minutes for the electrodes to reach equilibrium and for the meter reading to stabilize.
17. Read and record the pH value to 0.01 pH unit.
18. Recalibrate the meter between sample measurements if possible.

If you measure several samples of similar pH, do no more than three measurements; measuring more samples without recalibration may increase variability of the system. If you measure samples of widely differing pH (e.g., 7.5 and 12), recalibrate between samples.

If you measure more than one sample, always calibrate the meter after the final sample to check that no malfunction occurred during measurement. If you have difficulty calibrating the meter or if the slope value is not within tolerances, remeasure any samples read since the last calibration.

* Condensed from the complete laboratory version used in Kodak facilities. Contact your Kodak sales representative for more information on the complete method.

Electrode Care

Follow the manufacturer's recommendations for electrode care. Use pH 7 calibrating buffer for glass-electrode storage, and 3.5 M potassium chloride solution for reference-electrode storage. For temporary storage of the electrode pair between measurements, use the pH 7 storage buffer (0.1 M potassium chloride in pH 7 buffer).

Glass Electrodes—Preconditioning/Rejuvenation

Follow the manufacturer's recommendations for preconditioning glass pH electrodes. A minimum soaking time of 2 hours in pH 7 calibrating buffer is recommended before use for pH measurement; overnight soaking is better.

If an electrode fails to meet the slope tolerances or cannot achieve the assigned buffer values, use the following rejuvenating procedure:

1. Detach the electrode leads from the meter.
2. Place the glass electrode tip (detach the electrode lead from the pH meter during this process) in 1.0 M hydrogen chloride (R-1, S-3, F-0, C-0) for 5 minutes. Then place the same electrode in 1.0 M sodium hydroxide (R-1, S-3, F-0, C-0) for 5 minutes. Return the electrode to 1.0 M hydrogen chloride for another 5 minutes.
3. Soak the electrode in the pH 7 calibrating buffer for 2 hours.
4. Reconnect the electrode and try to calibrate it. If there is no improvement, discard the electrode.

Note: More severe reconditioning procedures are not recommended due to the toxicity of reagents required and the cost in analyst time versus the cost of electrode replacement.

5. If there is an improvement, but the electrode is still not reading the required values, repeat the sodium or potassium hydroxide and hydrochloric acid soaks, and try to calibrate it again. If there is no improvement, discard the electrode.

Reference Electrode—Care/Rejuvenation

Sleeve-type junction reference electrodes are the most accurate. However, due to the high flow rate of filling solution, close attention is required to ensure that the electrode has adequate filling solution, and that the electrolyte does not drain completely into the sample being measured. This is necessary for proper electrode performance and to avoid sample contamination.

Before installing a new reference electrode, withdraw the filling solution and refill the electrode with 3.5 M potassium chloride solution. At the beginning of each shift or day, withdraw the potassium chloride filling solution with a fine-tipped eyedropper and refill the electrode with fresh 3.5 M potassium chloride solution.

If substituting a new glass electrode does not improve the performance of the pH system, reference-electrode junction clogging may be the problem, especially when the pH readings are unsteady or inaccurate. If the filling solution has become contaminated, refill the electrode with fresh solution and recheck the system. Check frit-type junctions for flow by *gently* pressing the tip of the reference electrode against a paper towel several times. A small wet spot will be visible if the junction is flowing.

Clear a clogged calomel reference electrode by soaking the electrode junction for 1/2 hour in a warm solution (not above 50°C [122°F]) of 3.5 M potassium chloride diluted 1:9 with distilled water. Drain the electrolyte and replace the solution with fresh 3.5 M potassium chloride solution. Retest the electrode.

For clogged Ag/AgCl reference electrodes, use a 10-minute soak in 10-percent ammonium hydroxide solution to remove precipitated silver chloride from the junction. The electrode **must** contain filling solution during this procedure. **Do not** use higher concentrations of ammonium hydroxide solution or longer periods of soaking, because you may damage the reference element in some types of Ag/AgCl reference electrodes.

CAUTION: AMMONIUM HYDROXIDE IS

CORROSIVE. Ammonium hydroxide requires careful handling. See the Material Safety Data Sheet for handling and precautionary information. Observe *all* CAUTION statements. Avoid contact with skin or clothing by solution or vapors. Use a ventilation hood to avoid exposure to vapors. **Do not** weigh this chemical in an aluminum container.

As with glass electrodes, more severe rejuvenation procedures are not recommended because they are costly, and may result in more electrode damage than improvement in performance.

