KODAK Q-LAB Process Monitoring Service

PROCESS CONTROL HANDBOOK • Z-6

Color Developer

When film enters the color developer, the reversal agent absorbed by the emulsion in the reversal bath chemically exposes the unexposed silver halide. The color developing agent then reacts with the silver halide to form metallic silver. (The metallic silver image formed in the *first* developer is not a part of the reaction that takes place in this step.)

FUNCTIONS

- The color developer acts on the chemically exposed silver halide to form a positive silver image.
- As the metallic silver image is formed, the oxidized color developing agent reacts with the color couplers in each of the three layers of the film to form colored dyes. The dyes form only at the sites where the image is being converted to metallic silver.

COMPONENTS

Developing Agent:

KODAK Color Developing Agent CD-3

The developing agent acts on the chemically exposed silver halide to form metallic silver (equation 1, below). The oxidized developing agent reacts with adjacent dye couplers to form dye images (equation 2); it also reacts with competing chemicals (CZA and sulfite) to form soluble by-products (equations 3, 4).

- (1) $Ag^*X + CD-3 \rightarrow Ag^0 + X^- + CD-3^{ox}$
- (2) CD-3 $^{\text{ox}}$ + coupler \rightarrow Image dye (pH-sensitive)
- (3) CD-3^{$\circ x$} + CZA \rightarrow Soluble dye
- (4) CD-3 $^{\circ x}$ + sulfite \rightarrow Sulfonated CD-3 (soluble)

 $CD-3^{OX} =$ oxidized color developing agent CZA = citrazinic acid

Competing Chemicals:

Citrazinic acid (CZA) Sodium sulfite

Sulfite acts primarily as a preservative to protect the developing agent from oxidation, but it also reacts with oxidized developing agent as a competing chemical (equation 4).

The concentration of CZA and sulfite affects film contrast. Low concentrations produce an increase in contrast and D-max. High concentrations produce low upper-scale contrast.

The KODAK Sulfite Test Kit, Process E-6, enables you to measure the concentration of sulfite in your Process E-6 color developer and detect changes in the concentration *before* they affect the film you process. For example, as sulfite concentration increases, film contrast will be lower, especially in the high densities. As sulfite concentration decreases, film contrast will be higher, especially in high-density areas. Instructions for using this kit are given on page 10-4.



 $Ag^*X = chemically exposed silver halide$

CD-3 = color developing agent

 $Ag^{o} = metallic silver$

 X^{-} = halide ion

Preservative:

Sodium sulfite

Sodium sulfite helps to protect the color developing agent and CZA from oxidation. When the developer is oxidized rapidly, CZA will be oxidized slightly faster than the developing agent and film contrast will increase.

Silver Halide Solvent:

KODAK Silver Halide Solvent, HS-104

This solvent helps to accelerate the development reaction and helps to control the graininess of the final image. It is not consumed in the reaction, but it is subject to oxidation.

Buffer/pH:

Phosphate

Phosphate in the form of phosphoric acid is added to the concentrate to control pH. High and low pH values affect the reaction of couplers differently. A high pH produces cyan-green color-balance shifts. A low pH produces magentared color-balance shifts. (See page 6-8 for information on adding sulfuric acid or sodium hydroxide to optimize your process.)

Halide Salts:

Sodium bromide Potassium iodide

Bromide and iodide are by-products of the development reaction. Normal variations in concentration have little photographic effect in the color developer.

Sequestering Agent:

KODAK Anti-Calcium, No.4

As in the first developer, this chemical prevents precipitation of calcium and magnesium salts to ensure solution cleanliness.

Sensitometric Effects of Solution Component Concentration

The following tables list the effects on processed film of high and low concentrations of color-developer solution components.

HIGH CONCENTRATION

Solution Component	Sensitometric Effect
KODAK Color Developing Agent, CD-3	Increase in contrast and D-max
CZA	Lower upper-scale contrast with larger shift in green
Sodium sulfite	Lower upper-scale contrast
KODAK Silver Halide Solvent, HS-104*	Lower contrast
Sodium bromide†	Very slight decrease in D-max
Potassium iodide†	
Phosphate	Little to none
KODAK Anti-Calcium	Little to none

LOW CONCENTRATION

Solution Component	Sensitometric Effect
KODAK Color Developing Agent, CD-3	Decrease in contrast and D-max (very low CD-3 will produce red D-max)
CZA	Higher upper-scale contrast with larger shift in green
Sodium sulfite	Higher upper-scale contrast
KODAK Silver Halide Solvent, HS-104*	Higher contrast
Sodium bromide†	Slight increase in D-max
Potassium iodide†	
Phosphate	Little to none
KODAK Anti-Calcium	Little to none

*The concentration of this component is not as critical as CZA and sodium sulfite.

†The concentration of this component is not as critical in the color developer as it is in the first developer

Parameter	Aim	Tolerance	Acceptable Range	Plot Parameter
Time	6 minutes	±15 seconds	5 to 7 minutes	
Temperature	100.4°F (38°C)	±0.5°F (±0.3°C)	98 to 103°F (36.7 to 39.4°C)	Х
Replenishment Rate	200 mL/ft ² (2153 mL/m ²)	$\pm 20 \text{ mL/ft}^{2*}$ ($\pm 215 \text{ mL/m}^{2}$)*	_	Х
Specific Gravity				
Seasoned Tank Solution	1.038 at 80°F (27°C) 1.035 at 100.4°F (38°C)	±0.003	1.032 to 1.043 at 80°F (27°C) 1.029 to 1.040 at 100.4°F (38°C)	х
Fresh Tank Solution†	1.034 at 80°F (27°C) 1.031 at 100.4°F (38°C)	±0.003	1.027 to 1.038 at 80°F (27°C) 1.024 to 1.035 at 100.4°F (38°C)	
Replenisher	1.040 at 80°F (27°C) 1.037at 100.4°F (38°C)	±0.003	1.032 to 1.043 at 80°F (27°C) 1.029 to 1.040 at 100.4°F (38°C)	
Sulfite Concentration				
Seasoned Tank Solution	5.5 g/L	±0.5	4.5 to 6.0	Х
Fresh Tank Solution†	5.5 g/L	±0.5	4.5 to 6.0	
Replenisher	6.75 g/L	±05 —		
Agitation	2-second nitrogen burst every 10 seconds (⁵ / ₈ -inch [17 mm] solution rise)‡	_	_	

*For optimum performance, maintain your replenishment rate to within ± 5% of the specified aim (± 10% tolerance allows for measurement "noise").

†See the mixing instructions at the right. Plot the specific gravity and sulfite concentration of the new mix on Form Y-36. Note "NEW COLOR-DEVELOPER TANK MIX" on Form Y-33. ‡For rack-and-tank machines.

PREPARING A FRESH TANK SOLUTION

To prepare a fresh tank solution that will give results similar to those produced by a seasoned tank solution, follow the appropriate mixing instructions given below. (These instructions are different from those provided with the chemicals.) Following either procedure will help you obtain results closer to those produced at optimum process levels. You may need to make slight adjustments to optimize the process; see "Optimizing Your Process," page 6-7.

Note: These instructions are for mixing solutions from KODAK Color Developer Replenisher, Process E-6AR (5-gallon flexible container).

From Mixed Replenisher Solution

- 1. For each litre of tank solution, mix 850 mL of replenisher with 150 mL of water.
- 2. Add 5 mL of starter per litre of solution.

From Concentrate

- 1. For each litre of tank solution, mix 170 mL of Part A, 170 mL of Part B, and 660 mL of water.
- 2. Add 5 mL of starter per litre of solution.

Note: When you prepare the solution in either of these ways, the specific gravity and sulfite concentration will be within the tolerances for a fresh tank solution.

USING THE *KODAK* SULFITE TEST KIT, PROCESS E-6

Use this kit to measure the sulfite concentration in your Process E-6 color developer. Read these instructions before you run the test so that you are familiar with the procedure. To obtain accurate results, *follow these instructions exactly* and use good laboratory techniques.

Use only distilled water as required in the procedure. (Your results will be unreliable if you use other types of water [e.g., demineralized, deionized, tap, etc].)

Note: To run this test, you will use a procedure called a titration. A titration is a quantitative chemical analysis of a solution.

When you perform a titration, you determine the concentration of a certain chemical component (e.g., sulfite) of a solution sample by adding a standardized solution called a titrant—that causes a chemical reaction. Iodate iodide solution is the titrant used for this test.

The titrant first reacts with the chemical component that you are measuring. When the initial reaction is complete, the titrant then reacts with an indicator or another chemical in the solution to cause the color of the sample to change. The color change marks the end point of the reaction. It is important to stop adding titrant as soon as the reaction reaches the end point.

- 1. Fill the flask to the 30 mL line with distilled water.
- 2. Add the contents of two Dissolved Oxygen 3 Reagent Powder Pillows to the flask. Swirl the flask for 10 to 15 seconds to mix the powder and the water; some of the powder may not dissolve.
- 3. Add the contents of one Sulfite 1 Reagent Powder Pillow to the flask. Swirl the flask for 10 to 15 seconds to dissolve the powder.

- 4. Remove 1.0 mL of color-developer tank solution with the TenSette Pipet, and add it to the flask. Swirl the flask.
- 5. Use the digital titrator (with the counter reset to zero) with the lodate lodide Titration Cartridge to titrate the solution in the flask. Add titrant and swirl the flask until the solution **begins** to turn blue; determine the end point when the solution becomes blue and *remains* blue after you swirl it continuously for 5 to 10 seconds. *Be careful that you do not titrate the solution beyond the end point.*
- 6. Read the number from the digital counter.
- 7. To determine the sulfite concentration, use the titrator reading in the equation below or with the following table.

Color-developer = Titrator reading x 0.0315

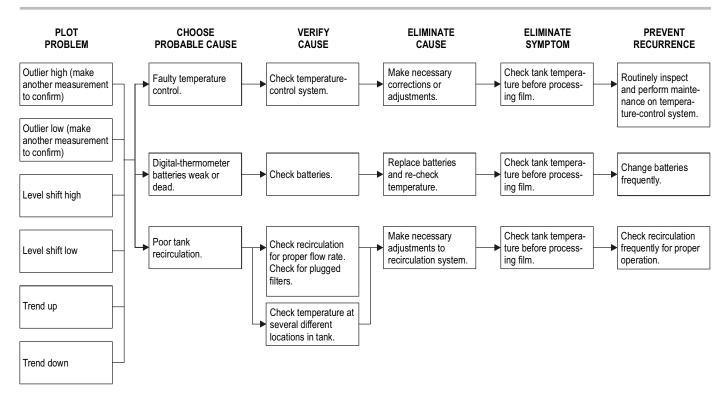
COLOR-DEVELOPER SULFITE CONCENTRATION						
Titrator Reading	Concentration (g/L)	Titrator Reading	Concentration (g/L)	Titrator Reading	Concentration (g/L)	
130	4.1	155	4.9	180	5.7	
131	4.1	156	4.9	181	5.7	
132	4.2	157	4.9	182	5.7	
133	4.2	158	5.0	183	5.8	
134	4.2	159	5.0	184	5.8	
135	4.3	160	5.0	185	5.8	
136	4.3	161	5.1	186	5.9	
137	4.3	162	5.1	187	5.9	
138	4.3	163	5.1	188	5.9	
139	4.4	164	5.2	189	6.0	
140	4.4	165	5.2	190	6.0	
141	4.4	166	5.2	191	6.0	
142	4.5	167	5.3	192	6.0	
143	4.5	168	5.3	193	6.1	
144	4.5	169	5.3	194	6.1	
145	4.6	170	5.4	195	6.1	
146	4.6	171	5.4	196	6.2	
147	4.6	172	5.4	197	6.2	
148	4.7	173	5.4	198	6.2	
149	4.7	174	5.5	199	6.3	
150	4.7	175	5.5	200	6.3	
151	4.8	176	5.5	201	6.3	
152	4.8	177	5.6	202	6.4	
153	4.8	178	5.6	203	6.4	
154	4.9	179	5.6	204	6.4	

- 8. Calculate and plot your variation from aim on Form Y-36; see "Using Forms Y-34, Y-35, and Y-36" on page 4-13 for more information. Check the plots of sulfite concentration for outliers, shifts, trends, and cycling to determine the state of control. If you detect an out-ofcontrol condition, refer to the diagnostic charts on pages 10-10 and 10-12.
- 9. Discard the solution from the flask, and rinse the flask thoroughly with distilled water. Remove the tip from the pipet and discard it.

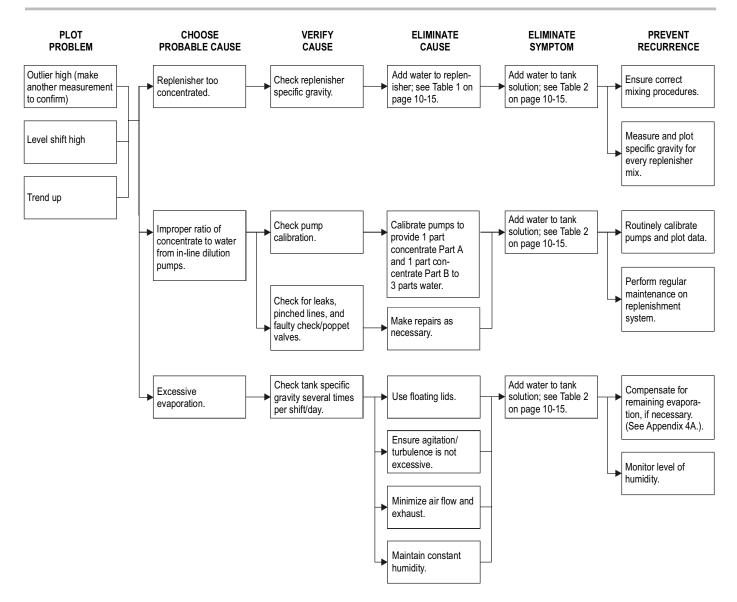
DIAGNOSTIC CHARTS

The diagrams on pages 10-5 to 10-13 provide you with a step-by-step approach to diagnosing process problems; they include the most common causes of problems. They are organized according to the appearance of your control plots for the key parameters for color developer. The recommendations in the charts will help you correct outliers (data on or outside the tolerance lines), level shifts, trends, and cycling. For more information on evaluating control-chart plots, see *Process Control— A Better Way*, Section 1.

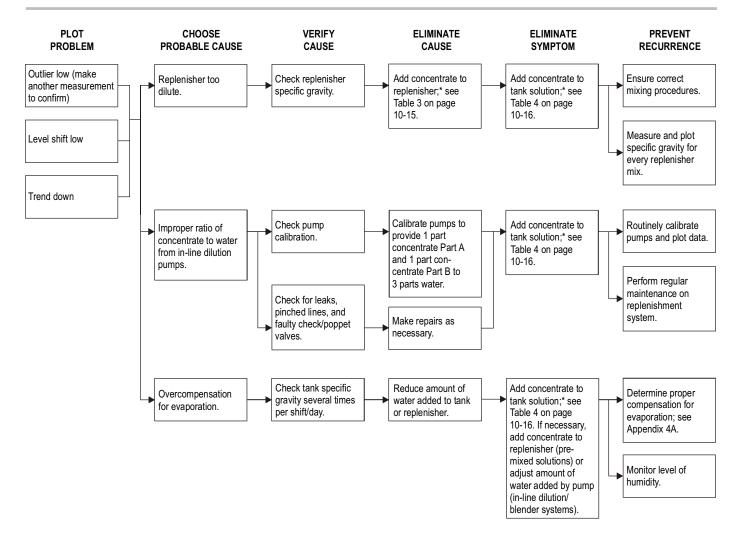
COLOR DEVELOPER—TEMPERATURE— Outlier High or Low, Level Shift High or Low, Trend Up or Down



COLOR DEVELOPER—SPECIFIC GRAVITY— Outlier High, Level Shift High, Trend Up

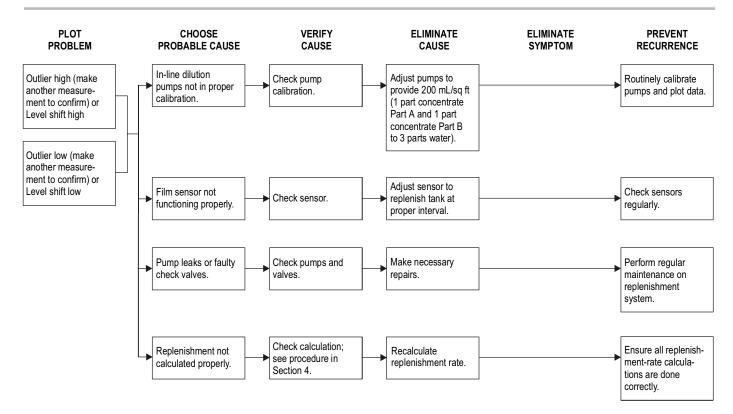


COLOR DEVELOPER— SPECIFIC GRAVITY— Outlier Low, Level Shift Low, Trend Down

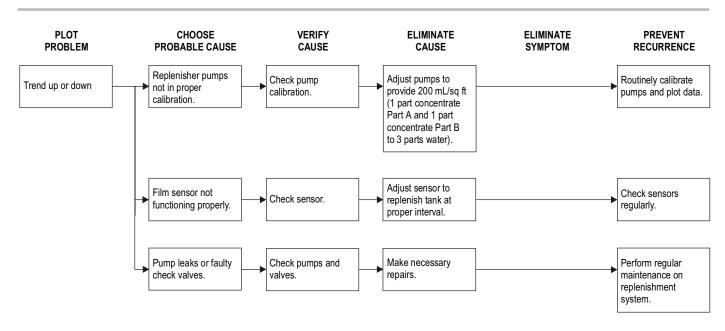


* Always add equal amounts of Part A and Part B when you add concentrate to adjust specific gravity.

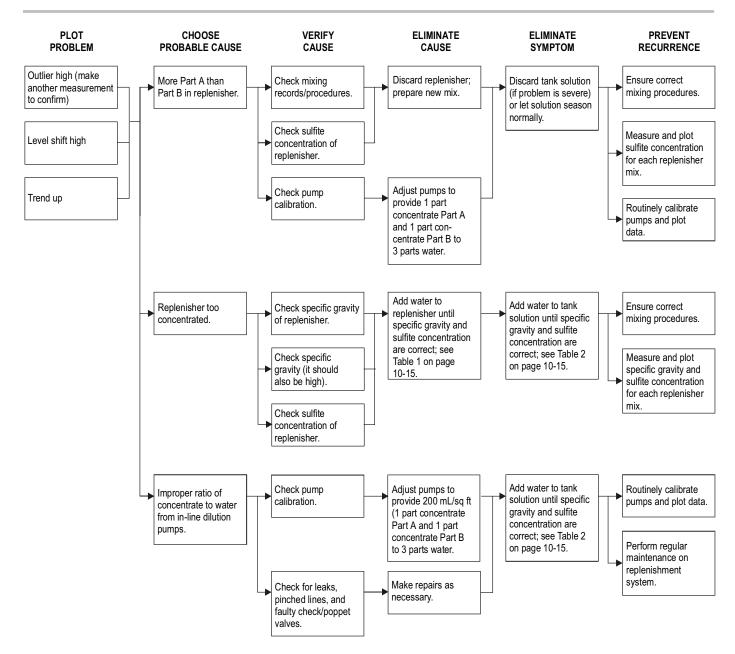
COLOR DEVELOPER—REPLENISHMENT RATE— Outlier High or Low, Level Shift High or Low



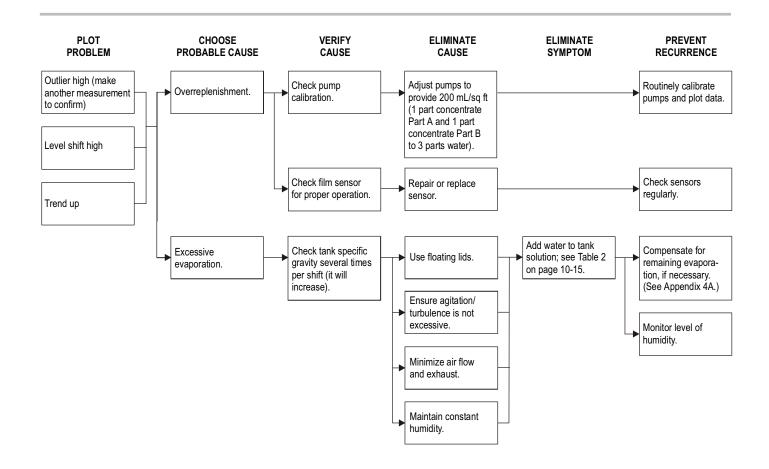




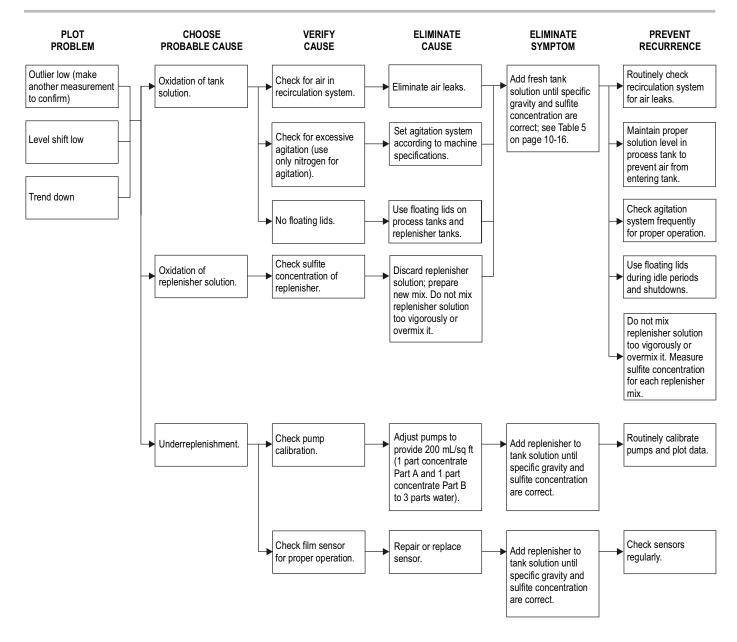
COLOR DEVELOPER—SULFITE CONCENTRATION— Outlier High, Level Shift High, Trend Up



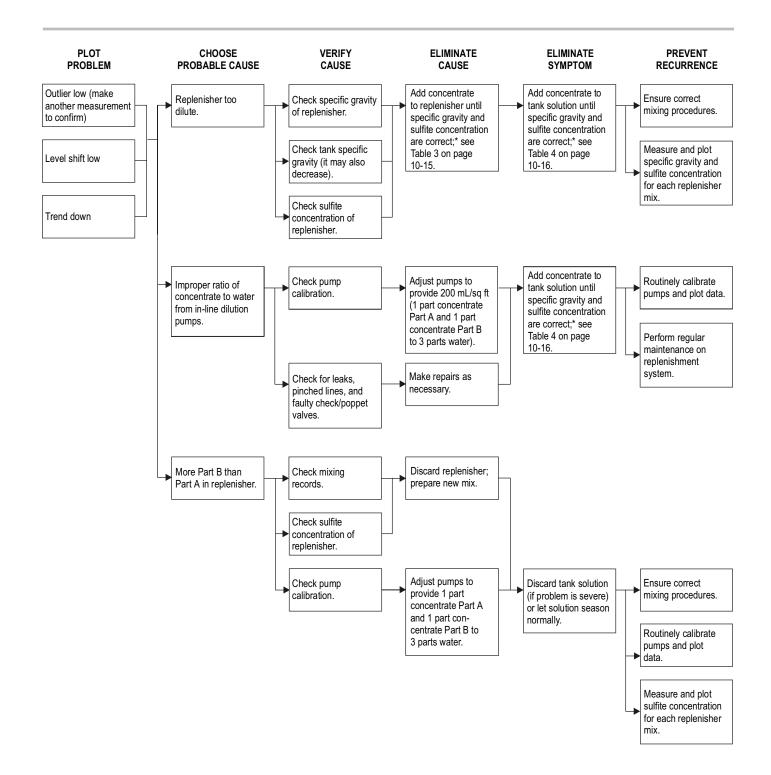
(Continued on next page)



COLOR DEVELOPER—SULFITE CONCENTRATION— Outlier Low, Level Shift Low, Trend Down



(Continued on next page)



* Always add equal amounts of Part A and Part B when you add concentrate to adjust sulfite concentration.

COLOR DEVELOPER— Cycling

TEMPERATURE

Look for a relationship between cycling and events that occur regularly:

- Start-up on Monday mornings
- Power-supply fluctuations in the lab during the day/week
- Large replenisher additions right before the temperature is measured

Make corrections or adjustments to eliminate the cause of cycling.

SPECIFIC GRAVITY

Look for a relationship between cycling and events that occur regularly:

- Start-up on Monday mornings
- Shift/operator changes
- Use of new replenisher mixes (check mixing procedures)
- Intermittent use of air conditioning

Check that you are compensating for evaporation correctly (see the procedure given in Appendix 4A, "Compensating for Evaporation"). Make specific-gravity measurements every 2 to 4 hours for 2 or 3 days to determine the cause of cycling.

Make corrections or adjustments to eliminate the cause of cycling.

REPLENISHMENT RATE

Look for a relationship between cycling and events that occur regularly:

- Shift/operator changes
- Power-supply fluctuations in the lab during the day/week
- Fluctuations in machine utilization Make corrections or adjustments to eliminate the cause of cycling.

SULFITE CONCENTRATION

Look for a relationship between cycling and events that occur regularly:

- Shift/operator changes
- Measurements made by different operators
- Use of new replenisher mixes (check mixing procedures) Make corrections or adjustments to eliminate the cause of cycling.

TABLE 1 Addition of Water to Correct for <i>Overconcentration</i> of Replenisher Solution			TABLE 2 Addition of Water to Correct for <i>Overconcentration</i> of Seasoned Tank Solution				
Specific Gravity Measured at 80°F (27°C)	mL of Water per Litre of Replenisher Solution	Specific Gravity Measured at 100.4°F (38°C)	mL of Water per Litre of Replenisher Solution	Specific Gravity Measured at 80°F (27°C)	mL of Water per Litre of Tank Solution	Specific Gravity Measured at 100.4°F (38°C)	mL of Water per Litre of Tank Solution
1.040	0	1.037	0	1.038	0	1.035	0
1.041	23	1.038	23	1.039	24	1.036	24
1.042	44	1.039	44	1.040	47	1.037	47
1.043	65	1.040	65	1.041	68	1.038	68
1.044	85	1.041	85	1.042	89	1.039	89
1.045	104	1.042	104	1.043	109	1.040	109
1.046	122	1.043	122	1.044	128	1.041	128
1.047	140	1.044	140	1.045	146	1.042	146
1.048	157	1.045	157	1.046	163	1.043	163
1.049	173	2.045	173	1.047	180	1.044	180
1.050	189	3.045	189	1.048	196	1.045	196

TABLE 3

Addition of Color-Developer Concentrate to Correct for *Underconcentration* of Replenisher Solution

Specific Gravity Measured at 80°F (27°C)	mL of Part A Concentrate per Litre of Replenisher Solution	mL of Part B Concentrate per Litre of Replenisher Solution	Specific Gravity Measured at 100.4°F (38°C)	mL of Part A Concentrate per Litre of Replenisher Solution	mL of Part B Concentrate per Litre of Replenisher Solution
1.040	0	0	1.037	0	0
1.039	8	8	1.036	8	8
1.038	15	15	1.035	15	15
1.037	23	23	1.034	23	23
1.036	30	30	1.033	30	30
1.035	37	37	1.032	37	37
1.034	44	44	1.031	44	44
1.033	50	50	1.030	50	50
1.032	57	57	1.029	57	57
1.031	63	63	1.028	63	63
1.030	69	69			

Seasoned Tank Solution					
Specific Gravity Measured at 80°F (27°C)	mL of Part A Concentrate per Litre of Tank Solution	mL of Part B Concentrate per Litre of Tank Solution	Specific Gravity Measured at 100.4°F (38°C)	mL of Part A Concentrate per Litre of Tank Solution	mL of Part B Concentrate per Litre of Tank Solution
1.038	0	0	1.035	0	0
1.037	8	8	1.034	8	8
1.036	15	15	1.033	15	15
1.035	22	22	1.032	22	22
1.034	29	29	1.031	29	29
1.033	36	36	1.030	36	36
1.032	43	43	1.029	43	43
1.031	49	49	1.028	49	49
1.030	55	55	1.027	55	55
1.029	61	61	1.026	61	61
1.028	67	67			
For each 40 mL of					

Addition of Color-Developer Concentrate to Correct for *Underconcentration* of Seasoned Tank Solution

TABLE 4

KODAK Color Developer Replenisher, Process E-6AR, Parts A and B, add 1 mL of KODAK Color Developer Starter, Process E-6

TABLE 5

Addition of Fresh Tank Solution to Correct for Low Sulfite Concentration Due to Oxidation of Tank Solution or Replenisher Solution

Sulfite Concentration (g/L Na ₂ SO ₃)	mL of Fresh Tank Solution per Litre of Tank Solution
4.3	500
4.5	439
4.7	405
4.9	342
5.1	242
5.3	138