3 MONITORING AND CONTROLLING PROCESSING SOLUTIONS

CONTROL OF PROCESS VARIABLES

Introduction

Process variables include process time, temperature, agitation, and replenishment and wash rates. Changing these variables affects the process in specific ways. Being aware of how each of these variables affects your process will help you to troubleshoot any problems, and to use these variables to make small adjustments in your process.

The specifications for these process variables are given in Table 3-1.

Table 3-1
Process E-6 Specifications

Step	Time (Minutes:Seconds)			Temperature °C (°F)			Replenishment Rate mL/m^2 (mL/ft^2)			Concentrate Ratio for Process E-6AR Chemicals (Concentrate:Water)
	Lower Limit	Aim	Upper Limit	Lower Limit	Aim	Upper Limit	Lower Limit	Aim	Upper Limit	
First Developer	5:00	6:00	7:00	36.7 (98.0)	38.0 (100.4)	39.4 (103.0)	1,938 (180)	2,153 (200)	2,368 (220)	1:4
First Wash	1:00	2:00	4:00	33.3 (92.0)	38.0 (100.4)	39.4 (103.0)	—	7.5 L/min (2 gal/min)	—	—
Reversal Bath	1:00	2:00	4:00	24.0 (75.0)	—	39.4 (103.0)	916 (85)	1,076 (100)	1,236 (115)	1:19
Color Developer	5:00	6:00	7:00	36.7 (98.0)	38.0 (100.4)	39.4 (103.0)	1,938 (180)	2,153 (200)	2.368 (220)	1:1:3
Pre-Bleach	2:00	2:00	4:00	24.0 (75.0)	—	39.4 (103.0)	916 (85)	1,076 (100)	1,236 (115)	1:9
Bleach	6:00	6:00	8:00	33.3 (92.0)	—	39.4 (103.0)	—	215 (20)	—	No dilution
Fixer	4:00	4:00	6:00	33.3 (92.0)	—	39.4 (103.0)	916 (85)	1,076 (100)	1,236 (115)	1:9
Final Wash*	4:00	4:00	8:00	33.3 (92.0)	—	39.4 (103.0)	—	7.5 L/min (2 gal/min)	—	—
Final Rinse	0:30	1:00	2:00	24.0 (75.0)	—	39.4 (103.0)	—	1,076 (100)	—	1:99

* For best results, use a countercurrent-flow final wash.

Process Temperature

Slight variations in developer solution temperature can affect process control. In other processing solutions, temperature variations of a few degrees are not as critical.

Once you have established the first- and color-developer temperatures, maintain them within these limits:

First Developer ±0.2°C (±0.3°F)

Color Developer ±0.3°C (±0.5°F)

Process Time

Time affects process control in about the same way that temperature does. It is particularly critical for the developers that you use the correct time. Use a stopwatch to measure the time that the film is in a solution from the time the film enters the solution to the time it enters the next solution (or wash).

Once you have established the first- and color-developer times, maintain them within these limits:

First Developer ±5 seconds

Color Developer ±5 secondsvM

Agitation

Agitation increases solution activity by removing used solution from the film surface and replacing it with fresh solution. Too little agitation causes streaks or spots on the film. Too much agitation mixes air into the solution, causing some of the chemicals to oxidize. Oxidation is particularly harmful to the first and color developers. Two common methods of producing solution agitation are: 1) moving the film through the solution, and 2) moving the solution over the film surface. The first method is used in continuous, roller-transport, and rotary-tube processors, and in sink-line processes (with manual agitation). The second method is used in rack-and-tank processors and in some continuous processors, as well as in sink-line processes. It consists of bubbling an inert gas (i.e., nitrogen for developers, air for other solutions) through the solution.

Table 3-2
Methods of Agitation

Step	Continuous, Roller-Transport, Rotary-Tube Processors, and Sink-Line Processes (with Manual Agitation)	Rack-and-Tank Processors and Sink-Line Processes
First Developer	Movement of film through the solution provides some agitation; slow speed machines may require supplemental agitation	Nitrogen
Wash		Air
Reversal Bath		None
Color Developer		Nitrogen
Pre-Bleach		None
Bleach*		Air
Fixer		Air
Wash		Air
Final Rinse		None

* Aeration is required for all types of processing.

Recirculation

Recirculation keeps the processing temperature uniform throughout the processing solution. To maintain uniform temperature, concentration, and solution cleanliness, you must recirculate the first developer, color developer, bleach, and fixer solutions. Recirculate the reversal bath, pre-bleach, and final rinse *only* as needed.

Filtration

Processing solutions and wash water may contain some insoluble solids and tars. If you don't remove this material, it can adhere to the film and to tank walls, rollers, and lines, and damage the film. Filters should be able to remove 10- to 30-micron-size particles from processing solutions and 5- to 25-micron-size particles from wash water.

Table 3-3 lists the filter materials available; it also lists if they are recommended for use with KODAK Chemicals, Process E-6.

Table 3-3
Filter Materials

Recommended	Not Recommended
Bleached cotton	Fiberglass with phenolic binder
Cellulose with phenolic resin binder	Polyester with phenolic resin binder
Polyester fiber	Wool with phenolic resin binder
Polypropylene	Viscose rayon with phenolic resin binder
Spun polypropylene	Viscose rayon

Polypropylene is the most acceptable filter-core material and one of the least expensive. However, many polypropylene yarns are produced by using surfactants. While polypropylene itself appears to have no photographic effect, some of these surfactants may; therefore, monitor your process carefully when you first change filters.

Replenishment

During processing, some chemicals in the processing solution are used up, and some chemicals in the film dissolve into the solution. These changes exhaust the solution. To compensate for these changes, and restore the solution's normal activity, you add replenisher solution. The rate at which you add replenisher solution affects the solutions's composition and activity.

You can add replenisher in one of four ways:

- By replenishing for a batch of film processed; add replenisher in a single amount after processing a batch of film.
- By feeding concentrate and water in simultaneously as a batch of film is processed.
- By continuously feeding replenisher in at a set rate during processing.
- By continuously feeding concentrate and water in simultaneously at a set rate during processing. This is similar to the third method, but the concentrate and the water are metered in separately instead of mixing the chemicals beforehand.

It is important that you calibrate and check all replenisher pumps and flowmeters frequently to be sure they are providing the correct amount of solution (or water).

Use only the rates recommended, especially with the developers. Initially, incorrect replenishment rates may not appear to affect your control plot, but eventually the effect will be significant. Also, image structure (graininess, sharpness, color quality, etc) can be affected without much change in the control plots. The problem may be more apparent in your production than in the control strip.

Wash-Water Control

Maintain the wash-water temperature and flow rate according to the recommended steps and conditions for your processor. A low flow rate or incorrect temperature in the first wash can cause speed and color-balance changes, and poor dye stability.

Do not use a wash between the reversal bath and color developer or between the pre-bleach and bleach. Replace water filters regularly to reduce dirt in the wash water. Use a flowmeter to be sure that you are using the correct water flow rate. To minimize algae formation, drain the wash tanks each night (or at the end of the final shift), and especially over weekends and holidays.

Drying

Film drying is influenced by the design of the dryer, time in the dryer, the pattern of air flow, the amount of final rinse carried into the dryer, and the humidity and temperature of the air in the dryer. Film drying can also be influenced by the ambient temperature and relative humidity. You must determine the optimum conditions for drying film for each processor. When your dryer is set correctly, the film will be dry when it is approximately one-half to three-quarters of the way through the dryer.

Do not use drying temperatures higher than 63°C (145°F). High drying temperatures cause excessive film curl. Filter the air in the dryer to reduce dirt. If the film has spots or streaks after drying, check for problems in the final rinse solution.

Checklists

Routine use of a start-up and shutdown checklist will help you keep your processor in good operating condition. Also, use your process maintenance checklist to follow a regular processor-maintenance schedule. For information about maintenance, see section 11.

COLOR-BALANCE CONTROL

Adjusting the pH

If your process is in control for the LD step, but has a green or magenta spread in the HD step, you can correct it by adjusting the pH of the color-developer tank solution with base (5N NaOH) or acid (5N H2SO4 or 28% acetic acid); see Table 3-4.

Table 3-4
Color-Developer pH Adjustments for Color-Balance Change

Color Balance Compared to the Reference Strip	Control Plot	Add to Tank Solution	To Change the Color Balance
Magenta	Green density plots *above* the red and blue densities for the HD step	1 mL/L of sodium hydroxide (5N NaOH)	.02
Green	Green density plots *below* the red and blue densities for the HD step	1 mL/L of sulfuric acid (5N H_2SO_4) or 1 mL/L of 28% acetic acid	.02

Preparing Sodium Hydroxide Solution

Warning

Follow the precautions for safe handling on the container label. Sodium hydroxide is corrosive; avoid contact with skin and clothing. Wear safety goggles, rubber gloves, and protective clothing. **Do not** weigh sodium hydroxide in an aluminum dish.

To prevent a violent reaction (boiling and splattering), always add the sodium hydroxide to the water; **never** add the water to the sodium hydroxide. With extreme caution and constant stirring, slowly add 200 grams of sodium hydroxide (NaOH) to 500 mL of cold water in a 2-litre glass beaker. Cool the solution to room temperature and add water to make 1 litre. Store this solution in a glass bottle with a rubber stopper or in a plastic (polyethylene) bottle, and label the bottle clearly.

Preparing Sulfuric Acid Solution

Warning

Follow the precautions on the container label. Sulfuric acid is corrosive; avoid contact with skin and clothing. Wear safety goggles, rubber gloves, and protective clothing.

To prevent a violent reaction (boiling and splattering), always add the sulfuric acid to the water; **never** add the water to the sulfuric acid. With extreme caution and constant stirring, slowly add 139 mL sulfuric acid H_2SO_4 (36N) to 700 mL of cold water in a 2-litre glass beaker. Cool the solution to room temperature and add water to make 1 litre. Store this solution in a glass bottle with a glass stopper, and label the bottle clearly.

MONITORING WITH SPECIFIC-GRAVITY MEASUREMENTS

Definition

Measuring specific gravity is a quick way of checking for proper mixing of your solutions. You can also make adjustments to your solutions by using specific-gravity measurements.

Specific gravity is the ratio of the mass of a liquid to the mass of an equal volume of water. It is a convenient way to measure the total dissolved material in a solution and check the concentration of processing solutions. Use specific-gravity measurements to check for mixing errors or water evaporation from solutions. There are three ways that you can use specific-gravity measurements for process control.

- To check for errors in mixing fresh tank and replenisher solutions (see section 2, “Chemicals and Chemical Mixing”).
- To check tank solutions for evaporation (see section 4, “Starting Up Your Process”).
- To adjust the concentration of your color-developer tank solution to optimize the process for contrast (see section 4, “Starting Up Your Process”).

Table 3-5 lists the specific-gravity aims for Process E-6 replenisher solutions and fresh tank and seasoned tank solutions.

Table 3-5
Specific-Gravity Aims

Solution	Specific Gravity Measured at 27°C (80°F)			Specific Gravity Measured at 38°C (100.4°F)		
	Replenisher	Fresh Tank	Seasoned Tank	Replenisher	Fresh Tank	Seasoned Tank
KODAK PROFESSIONAL First Developer	1.057 ±0.003	1.055 ±0.003	1.060 ±0.003	1.054 ±0.003	1.052 ±0.003	1.057 ±0.003
KODAK PROFESSIONAL Reversal Bath	1.006 ±0.003	1.004 ±0.003	1.005 ±0.003	1.002 ±0.003	1.001 ±0.003	1.002 ±0.003
KODAK PROFESSIONAL Color Developer	1.040 ±0.003	1.034 ±0.003	1.038 ±0.003	1.037 ±0.003	1.031 ±0.003	1.035 ±0.003
KODAK PROFESSIONAL Pre-Bleach	1.019 ±0.003	1.019 ±0.003	1.021 ±0.004	1.016 ±0.003	1.016 ±0.003	1.018 ±0.004
KODAK PROFESSIONAL Bleach	1.260 ±0.010	1.130 ±0.010	1.190 ±0.070	1.257 ±0.010	1.127 ±0.010	1.187 ±0.070
KODAK PROFESSIONAL Fixer	1.041 ±0.003	1.041 ±0.003	1.065 ±0.025	1.038 ±0.003	1.038 ±0.003	1.062 ±0.025

Measuring Specific Gravity

You can make specific-gravity measurements of your solutions with any hydrometer that meets the standard ANSI/ ASTM E100-72. The hydrometer should be marked in increments of at least 0.001 for an accuracy of ±0.0005. Although most hydrometers are calibrated at 15.6°C (60°F), they are useful at other temperatures. To measure the specific gravity of Process E-6 solutions, you will need the standard hydrometers listed in Table 3-6.

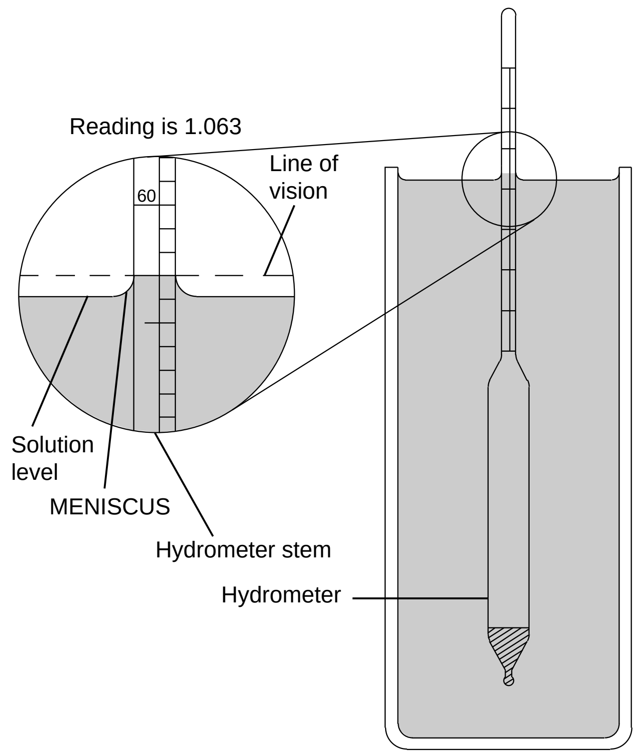
Table 3-6
Hydrometers for Process E-6 Solutions

Solution	Range of Standard Hydrometer	ASTM No.
First developer and replenisher	1.050 to 1.100	126H
Reversal bath and replenisher Color developer and replenisher Pre-Bleach and replenisher	1.000 to 1.050	125H
Bleach* and replenisher	1.100 to 1.150 1.150 to 1.200 1.200 to 1.250 1.250 to 1.300	127H 128H 129H 130H
Fixer* and replenisher	1.000 to 1.050 1.050 to 1.100	125H 126H

* More than one hydrometer is listed for bleach and fixer because the acceptable ranges of the specific-gravity measurements for these solutions are large.

Note: You should *not* need all six standard hydrometers listed in Table 3-6 for any one type of machine running Process E-6.

1. Fill a clean, dry 250 mL graduated cylinder to within 2.5 cm (1 inch) of the top with the solution you are measuring.
2. Adjust the solution to the proper temperature (see the specifications given in Table 3-5). *Proper solution temperature is very important.*
3. Place the cylinder in a sink or tray to catch overflow.
4. Choose the correct hydrometer to match the approximate specific gravity of the solution. (See the hydrometer ranges listed in Table 3-6.)
5. Be sure that the hydrometer is clean and dry. Carefully lower the hydrometer into the solution. Let it bob up and down slightly. When it stops, read the number at the **top** of the MENISCUS.



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6. After making the measurement, discard the sample. To avoid contaminating solutions, **do not** return the sample to the tank.
7. Rinse the hydrometer and graduated cylinder thoroughly with water.

Note: Never take specific-gravity readings of solutions in the tanks. If you use the wrong hydrometer, it can sink to the bottom of the tank and break, or bob on the surface, where the stem may hit the edge of the tank and break. Label hydrometer boxes to avoid confusion.

Do not use tape labels on the hydrometers.

Adjusting Your Processing Solutions by Using Specific-Gravity Measurements

First and Color Developers: The first and color developers are the most critical solutions in Process E-6; it is especially important to maintain proper concentrations.

You can use specific-gravity measurements to correct for overconcentration or underconcentration. A sample calculation for overconcentration is given below. In the example, the calculation is done by using the difference between the specific gravity of an overconcentrated solution and the specific-gravity aim. With this type of calculation, you can determine the amount of overconcentration. Or, you can use the values in Table 3-7 instead of making a calculation for overconcentrated first developer. To adjust the solution, remove and discard 8.6 litres of solution. Replace that amount of solution with the same amount of water. After the water is added, the specific gravity of the solution should be 1.060 ±0.003 (at 27°C [80°F])).

Example of a Specific-Gravity Calculation: You suspect that your first-developer tank solution is overconcentrated. You measure its specific gravity at 27°C (80°F); the specific gravity is 1.066. When you check Table 3-5, you note that the specific-gravity aim for a seasoned tank solution is 1.060 ±0.003. To correct the solution, you need to know the volume of the tank to calculate the amount of adjustment required. In this case, the tank volume is 95 litres. Sample calculations are as follows:

	Step	
A	Specific gravity of first-developer tank solution	1.066
B	Specific-gravity aim	1.060*
C	A minus B	0.006
D	A minus 1.000 (the specific gravity of water)	0.066
E	Amount of overconcentration (C divided by D)	0.091†
F	Volume of tank solution	95 L
G	Volume of water to add to tank solution (E multiplied by F)	8.6 L

* From Table 3-5
† 0.091 equals 9.1 percent overconcentration.

You can also adjust *underconcentrated* solutions by using specific-gravity measurements. If your first-developer tank solution is diluted by a water leak, you can adjust the solution by adding undiluted KODAK PROFESSIONAL First Developer Concentrate, Process E-6AR. To make the adjustment, measure the specific gravity. Then use Table 3-8 to determine the amount of first developer replenisher concentrate you need to add for each litre of tank solution. (Table 3-10 has information for adjusting seasoned color developer for underconcentration.) Finally, remove the amount of the underconcentrated solution you have determined in your calculation, and replace it with undiluted replenisher.

Table 3-7
Addition of Water to Correct for *Overconcentration* of First Developer—Seasoned Tank Solution

Specific Gravity at 27°C (80°F)	mL Water per Litre of Tank Solution	Specific Gravity at 38°C (100.4°F)	mL Water per Litre of Tank Solution
1.060	0	1.057	0
1.061	16	1.058	16
1.062	31	1.059	31
1.063	45	1.060	45
1.064	60	1.061	60
1.065	74	1.062	74
1.066	87	1.063	87
1.067	100	1.064	100
1.068	113	1.065	113
1.069	125	1.066	125
1.070	137	1.067	137
1.071	149	1.068	149
1.072	160	1.069	160
1.073	171	1.070	171
1.074	182	1.071	182
1.075	192	1.072	192
1.076	203	1.073	203
1.077	212	1.074	212

Table 3-8
Addition of KODAK PROFESSIONAL First Developer Concentrate, Process E-6AR, to Correct for *Underconcentration* of Seasoned Tank Solution

Specific Gravity at 27°C (80°F)	mL of Concentrate per Litre of Tank Solution	Specific Gravity at 38°C (100.4°F)	mL of Concentrate per Litre of Tank Solution
1.060	0	1.057	0
1.059	5	1.056	5
1.058	9	1.055	9
1.057	14	1.054	14
1.056	19	1.053	19
1.055	23	1.052	23
1.054	28	1.051	28
1.053	32	1.050	32
1.052	36	1.049	36
1.051	41	1.048	41
1.050	45	1.047	45
1.049	49	1.046	49
1.048	54	1.045	54
1.047	58	1.044	58
1.046	62	1.043	62
1.045	66	1.042	66
1.044	70	1.041	70
1.043	74	1.040	74
1.042	78	1.039	78
1.041	82	1.038	82

For each 40 mL of undiluted First Developer Replenisher, Process E-6AR, add 1 mL of KODAK First Developer Starter, Process E-6

Table 3-9
Addition of Water to Correct for *Overconcentration* of Color Developer—Seasoned Tank Solution

Specific Gravity Measured at 27°C (80°F)	mL of Water per Litre of Tank Solution	Specific Gravity Measured at 38°C (100.4°F)	mL of Water per Litre of Tank Solution
1.038	0	1.035	0
1.039	24	1.036	24
1.040	47	1.037	47
1.041	68	1.038	68
1.042	89	1.039	89
1.043	109	1.040	109
1.044	128	1.041	128
1.045	146	1.042	146
1.046	163	1.043	163
1.047	180	1.044	180
1.048	196	1.045	196

Table 3-10
Addition of Undiluted KODAK PROFESSIONAL Color Developer Replenisher, Process E-6AR, *to Correct for Underconcentration* of Seasoned Tank Solution

Specific Gravity Measured at 27°C (80°F)	mL of Part A Concentrate per Litre of Tank Solution	mL of Part B Concentrate per Litre of Tank Solution	Specific Gravity Measured at 38°C (100.4°F)	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 undiluted KODAK PROFESSIONAL Color Developer Replenisher, Process E-6AR, Parts A and B, add 1 mL of KODAK PROFESSIONAL Color Developer Starter II, Process E-6

APPENDIX 1

HYDROMETER CROSSOVER PROCEDURE

Like other measuring instruments, hydrometers have an inherent variability. Although the variability from hydrometer to hydrometer is usually small, you should run a crossover test when you use a "new" hydrometer. To run a crossover test, follow these steps:

8. Make specific-gravity measurements of at least four different samples of the same tank solution with both the "old" and the "new" hydrometer.
9. Determine the average measurement for each hydrometer by adding the measurements and dividing the result by the number of readings.
10. To calculate the difference between the hydrometers, subtract the smaller average from the larger average.

If the difference between the average readings for the hydrometers is greater than 0.002, contact your Kodak account executive to help you determine which hydrometer is correct. If the difference is less than or equal to 0.002, start using the "new" hydrometer.

Note: Sample calculations are shown at the right.

Table 3-11
Example 1

Measurement	Reading with "Old" Hydrometer	Reading with "New" Hydrometer
1	1.063	1.062
2	1.062	1.062
3	1.063	1.063
4	1.062	1.063
5	1.064	1.064
Total	5.314	5.314

Average Reading—"old" hydrometer $\frac{5.314}{5} = 1.0628$

Average Reading—"new" hydrometer $\frac{5.314}{5} = 1.0628$

Difference = 1.0628 – 1.0628 = 0; use the "new" hydrometer.

Table 3-12
Example 2

Measurement	Reading with "Old" Hydrometer	Reading with "New" Hydrometer
1	1.063	1.066
2	1.062	1.065
3	1.061	1.064
4	1.062	1.066
5	1.064	1.066
Total	5.312	5.327

Average Reading—"old" hydrometer $\frac{5.312}{5} = 1.0624$

Average Reading—"new" hydrometer $\frac{5.327}{5} = 1.0654$

Difference = 1.0654 – 1.0624 = 0.003 > 0.002; contact your account executive to determine which hydrometer is correct.