

Complete Control of Developer Carbonate

by Lori L. McPherson

Yes, there are alternative make-up systems!

Proper control of carbonate developing solutions is critical to forming accurate, consistent circuit dimensions and resist sidewall shape. Controlling either sodium or potassium carbonate solutions by pH alone, however, cannot guarantee true carbonate concentrations. Equally important control factors are the initial developer concentration and an understanding of the buffered chemistry of a carbonate-bicarbonate-carbonic acid system.

THE CO_3^{2-} - HCO_3^- BALANCE

A carbonate start-up solution is continually converted to bicarbonate in the development process. As this occurs, the pH drops from approximately 11.2 to 10.3, indicating a depleted bath containing about 50% sodium carbonate. By feed-and-bleed replenishment with sodium carbonate, bath life is extended and consistent development is maintained.

Most photoresist manufacturers recommend a start-up concentration of 1% by weight, with a feed-and-bleed system controlled to a pH setpoint of 10.5 to 10.6, maintaining a minimum carbonate concentration of approximately 75% by weight. But if the initial make-up and the feed solutions are not maintained at 1%, the carbonate-bicarbonate relationship renders the 10.5 setpoint meaningless.

As shown in Figure 1, the relative amount of each form of dissolved carbonate varies logarithmically with pH, and equal concentrations of carbonate and bicarbonate exist at the

intersection of their lines at pH 10.33 (at 25°C, this value varies with temperature). If the initial concentration was 1.0 weight % carbonate, the concentrations of both carbonate and bicarbonate at pH 10.33 would be 0.5 weight %. However, if the initial concentration was 0.8%, the concentrations at 10.5 pH would be only 0.4%. If the make-up concentration is not accurately controlled, the pH measurement is meaningless.

CONTROLLING CO_3^{2-} MAKE-UP

Of the three ways to control carbonate make-up, the least accurate is adding a weighed amount of carbonate to a known volume of solution. But the difference between the anhydrous and monohydrate forms must be included in the make-up calculation. Sodium and potassium carbonates are usually sold as monohydrates in analyses after solution and in developer vendors' literature. Room for error exists in the calculations, weighing, and volume measurements.

In the second, more accurate, and time-consuming method, a grab sample of the developer solution is titrated in the laboratory to a double endpoint (8.3 and 4.3). Bicarbonate as well as carbonate can then be determined by subtracting the first endpoint results from the second.

The third method is an on-line conductivity measurement that translates directly to sodium or potassium carbonate concentration. A 1% solution

of either carbonate has an associated conductivity of 14,000M Ω (Figure 2). Many conductivity instruments read directly in % concentration of carbonate. All conductivity instruments can be easily calibrated with standard resistors or conductivity standard solutions. If the developer solution is made with softened water, the sensor will remain scale-free and require virtually no maintenance.

CONDUCTIVITY MEASUREMENTS

Conductivity measurement determines the current flowing through a solution at a standard potential. The size of the positive or negative ions that carry the current through the solution affects their mobility and ability to carry current. If the solution consists of a single set of positive and negative ions (Na^+ and CO_3^{2-}), conductivity can be directly related to the number of ions present and the chemical concentration. In the 1% range,

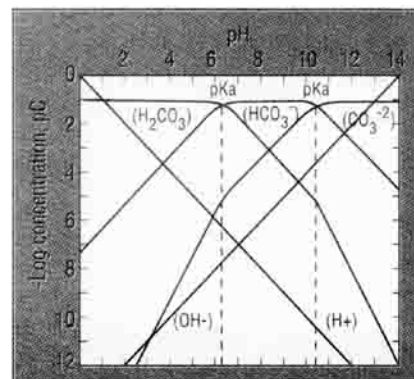


Figure 1. The pC-pH diagram for a carbonate solution, $C_{T,\text{CO}_3} = 1\text{M}$ at 25°C (approximately 1% by weight).

the relationship is very linear, and the concentration is easily interpreted from the conductivity measurement (At carbonate concentrations greater than 12%, the quantity of ions hinders their mobility and the linear relationship begins to drop off).

Conductivity measurement for carbonate concentration is only valid for the make-up and feed solutions when the chemical exists as a pure carbonate with essentially no bicarbonate or carbonic acid present. If a combination of carbonate and bicarbonate is present, as in the developer after resist has been dissolved, the instrument will read the combined conductivity of both. Then pH becomes the critical measurement in ensuring the initial 1% concentration does not fall below the desired level. ■

Lori L. McPherson is analytical product manager with George Fischer Signet, Tustin, CA.

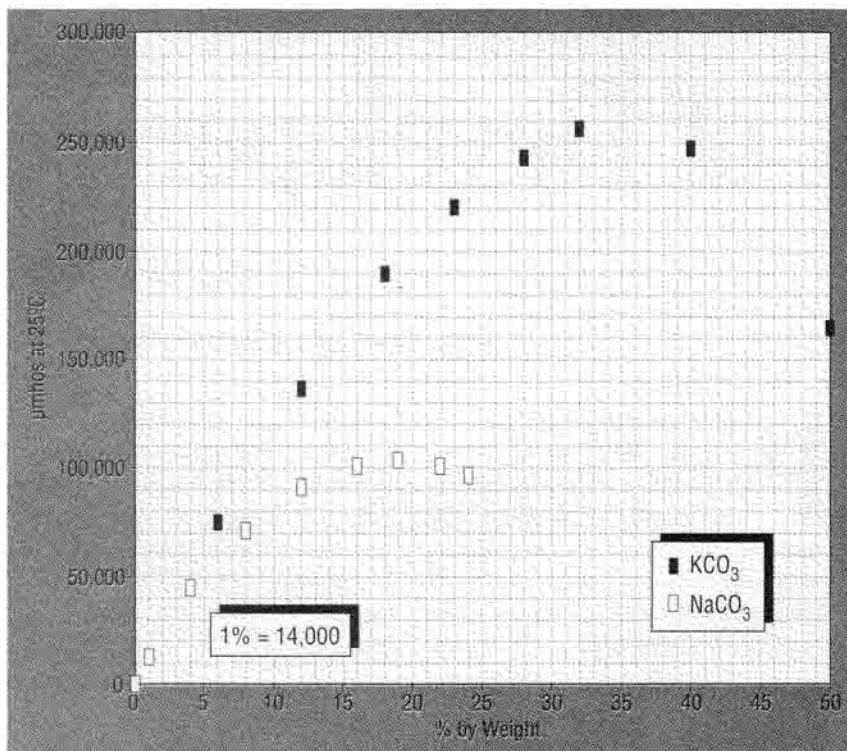


Figure 2. Conductivity vs. % concentration of carbonate.