DuPont Photopolymer & Electronic Materials

Printed Circuit Materials

# Determining Weight Percent Carbonate in Developer Solution

## Technical Bulletin TB-9947

### Developer Concentration

Sodium carbonate usually comes in powder form and is mixed with water before adding to the developer sump. Potassium carbonate, while available in powder form, is usually used as a liquid concentrate and diluted with water, usually in a feed and bleed system, before being added to the developer sump. All solid forms of carbonate will tend to pick up moisture from the air. Whether using solid or liquid, it is very important that the total carbonate concentration in the sump be maintained at a constant level as specified in the photoresist data sheet. Therefore, routine checks of the total carbonate concentration should be made, both when a fresh sump is made and on a routine basis if a feed and bleed system is used.

The total carbonate concentration in the developer sump can be easily measured by acid titration. The total carbonate concentration is the sum of the carbonate ("active carbonate") and bicarbonate that exist together in the developer sump. It is possible to measure both the total carbonate concentration and the portion of the total carbonate that is in the "active carbonate" (as opposed to the bicarbonate) form. Since the pH of the developer solution is proportional to the ratio of the "active carbonate" concentration to the bicarbonate concentration in the solution, measurement of the "active carbonate" is usually not necessary.

### Titration Procedure

The titration for total carbonate is accomplished by measuring the amount of acid needed to convert the "active carbonate" and bicarbonate in the developer solution to carbonic acid. A sample of the developer sump solution is taken and hydrochloric acid is used to reduce the pH of the solution to a lower pH that indicates that all the "active carbonate" and bicarbonate have been converted to carbonic acid. This is referred to as the pH endpoint. The endpoint can be measured either with a pH meter or with a pH indicator solution.

The pH endpoint for measuring "active carbonate" is 8.2. Phenolphthalein pH indicator solution is used to indicate this pH endpoint.

The pH endpoint for measuring the total carbonate is 3.2. Methyl Orange pH indicator solution is used to indicate this pH endpoint.

Procedures for each are given below. Since the measurement of total carbonate concentration is by far the more important, that procedure will be given first.

### Reagents Needed:

0.1 *N* Hydrochloric Acid (HCl)

0.1 % Methyl Orange solution

(Fisher Scientific #SM54)

1 % Phenolphthalein solution

(Fisher Scientific #SP62)

## Measurement of Weight Percent of Total Carbonate

1. Pipette 25.0 ml of developer solution into an Erlenmeyer flask.
2. Add 100 ml of DI water.
3. Add 5 drops of methyl orange to the solution. The color of the solution will be yellow.
4. Titrate with 0.1 *N* HCl. The endpoint is indicated by a color change to salmon/red. Record the volume of the acid required to reach the endpoint.
5. Calculations
   a. Vs is the sample volume in milliliters (25 mil)
   b. Va is the volume of the acid required to reach the endpoint in milliliters.
   c. *N* is the normality of the acid (0.1).
   d. FW is the formula weight of the carbonate used to make up the developer solution.
      Sodium Carbonate, (anhydrous) = 106
      Sodium Carbonate, (monohydrate) = 124
      Potassium Carbonate = 138

$$\text{wt\%} = \frac{N \times Va \times FW}{20 \times Vs}$$

### Example:

If the volume of 0.1 *N* HCl acid required to reach the endpoint is 40 ml, then the weight percent of sodium carbonate is as follows:

$$\frac{0.1 \times 40 \times 106}{20 \times 25} = 0.85 \text{ wt\% Sodium Carbonate(Soda Ash)}$$

## Measurement of Weight Percent Active Carbonate

1. Pipette 25.0 ml of developer solution into an Erlenmeyer flask.
2. Add 100 ml of DI water.
3. Add 5 – 7 drops of 1% Phenolphthalein to the solution. The color of the solution will be pink to red.
4. Titrate with 0.1 *N* HCl. The endpoint is indicated by a color change to colorless. Record the volume of the acid required to reach the endpoint.
5. Calculations
   a. Vs is the sample volume in milliliters (25 mil)
   b. Va is the volume of the acid required to reach the endpoint in milliliters.
   c. *N* is the normality of the acid (0.1).
   d. FW is the formula weight of the carbonate used to make up the developer solution.
      Sodium Carbonate, (anhydrous) = 106
      Sodium Carbonate, (monohydrate) = 124
      Potassium Carbonate = 138

$$\text{wt\%} = \frac{N \times Va \times FW}{10 \times Vs}$$

### Example:

Assume a developer sump is made up at 1.0% Potassium Carbonate as the total carbonate concentration. After developing some panels, some of the "active carbonate" will have been converted to bicarbonate. A sample is taken and the titration for "active carbonate" is done. If the volume of 0.1 *N* HCl required to reach the colorless Phenolphthalein endpoint is 14.5 ml, then the weight percent of "active carbonate" in the solution is 0.8%. Remember that the total carbonate concentration is still 1.0 wt.%.

It is possible to do both titrations by placing a pH probe in the solution and watching for the correct pH endpoint. The solution should be stirred using a magnetic stirrer or equivalent when doing the titration with a pH meter.

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