Tech Talk

Fine Lines in High Yield (Part CXLVI)

Resist Loading in Aqueous Developers

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To properly control the developer chemistry in a feed-and-bleed operation, the addition of fresh developer solution ("feed") needs to be tied to the rate of consumptior of carbonate, the active ingredient in the developer. There are a number of parameters one could monitor to trigger feed volume and addition time: resist loading, percent active carbonate, the ratio of carbonate to bicarbonate, or pH. Resist loading measurements are hardly ever used to control developer chemistry because a direct analysis e.g. of organic carbon is not straight forward. One could remove the inorganic carbon (carbonate) by acidification, but the resist will precipitate as a gooey mess. Photo-spectrometric methods have been tried with some success, but since loaded developer solutions are not clear, transparent solutions, there have always been questions about the validity of this method. Fortunately, there are parameters that are easier to measure and correlate well with resist loading as we will see. Figure 1 shows in Equation 1 the equilibrium between carbonate, bicarbonate and free caustic. Equation 2 shows the reaction of sodium hydroxide with the resist's carboxylic acid groups, forming soluble, or partially soluble, developed resist, which constitutes the "resist loading" in the developer. The same equilibria exist of course if potassium carbonate is used instead of sodium carbonate.

$$Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3 \qquad (1)$$

$$\text{—(CH}_2\text{CH)— with pendant O=C-O-H} + NaOH \rightleftharpoons \text{—(CH}_2\text{CH)— with pendant O=C-O-Na} + H_2O \qquad (2)$$

Resist binder's carboxylic acid group → Soluble sodium carboxylate salt

Figure 1: Equilibria in Developer Chemistry

Let us go back to the notion of resist loading. The concept of resist loading is a way of keeping track of the volume of resist that accumulates in the developer per unit volume of developer solution (Ref. 1, 2). One could express the volume of developed resist in cubic inches (or cubic centimeters). However, in a production environment it is more convenient to keep track of the square meters or square feet of boards processed. So the resist volume is typically tracked in "mil square foot" units. As long as we know the thickness of the resist, the number of mil square feet will be obtained by multiplying the number of square feet of developed resist by the number of mils of thickness of the resist. For example: starting with a fresh developer, 600 square feet of panel surface were processed, from which 50% of the resist was removed during development. The resist was a 2.0 mil thick plating resist. The resist loading is 600 mil square feet:

600 ft2 x (50%) = 300 ft2 of developed resist
300 ft2 x 2.0 (mils thickness) = 600 mil square feet.
Where metric units are the norm, resist loading has been measured in "micron meters square / liter", but also "mil square meters / liter". Conversions are as follows:

1 mil square foot / gallon = 0.623 micron meters square / liter
1 micron meter square / liter = 1.60 mil square feet / gallon.

As resist loading increases in a batch of developer solution active carbonate concentration drops. This makes the developer solution less aggressive and slows down the rate of development. It also reduces the pH of the solution. Figure 2 shows how increasing resist loading affects the time-to-clean (Tc) of the resist and the pH of the developer solution. The time-to-clean is short when the developer solution is fresh and most aggressive. At a loading of about 2 mil square feet per gallon, the time-to-clean becomes more stable, remaining fairly constant until about 12 mil square feet per gallon. As the loading becomes even higher the time-to-clean begins to increase rapidly. The pH drops rather sharply during the first 2 mil square feet of loading and then drops fairly linearly with loading.

Development will still be possible at very high loadings but it is typically not recommended for the following reasons. At high loadings the time-to-clean will be longer than normal and this means that the developer conveyor will have to run more slowly. As a result the total time that the resist remains in the developer solution will be much longer than usual. This long residence time is not good because it will result in some degree of attack of the sidewalls of the resist. A good rule of thumb for batch operation is to dump the developer when the pH reaches 10.2 or 10.3, depending on the resist being used. The recommendation for feed and bleed operation, is to set the pH control to 10.6 ± 0.1. While resist loading concentrations in the range of 6 to 12 mil square feet per gallon are typically recommended, note that the loading study described below, using carbonate with a small percentage of sodium hydroxide, found no detrimental effect at higher loadings within the limits of the study. Figure 2, a so called "loading curve" that may be obtained from the resist supplier, shows that for a recommended loading range of e.g. 6 to 12 mil square feet per gallon, time-to-clean does not shift much, nor does the pH, but the pH range is sufficiently large to allow feed-and-bleed control by pH. One could argue that there is no universal loading curve for all aqueous developable resists because the binders in different photoresists have different "acid numbers", an indicator of the number of carboxylic acid groups per unit weight of resist, a parameter that should translate into different loading curves. This is indeed the case, but for all practical purposes, the differences are not large enough to affect resist loading recommendations.

A plot of both pH and percent active carbonate (Figure 3) shows they track very well. From this we can conclude that pH is a very good predictor of the active carbonate in the developer solution. Similarly, the ratio of active carbonate to total carbonate (% active carbonate / % total carbonate) also can be predicted well from the pH of the solution.

For batch replenishment, the chemical composition of the developer is normally not monitored directly. The developer conveyor speed may be initially adjusted to give a breakpoint at the low end of the recommended range, followed by monitoring the breakpoint during operation, and dumping the developer once the upper end of the recommended range has been reached. Empirically, this control experience can then be translated into a predetermined resist throughput per volume developer solution, and a panel count can signal the need for a dump.

In recent years, suppliers of developer solution concentrates began to offer carbonate concentrates that contain a small percentage of caustic (see Ref. 3). If NaOH is added to increase bath life, bicarbonate is converted back to carbonate (Equation 1). This increases the pH, since pH correlates with the carbonate/bicarbonate ratio. This in essence "regenerates" the initial developer chemistry, permitting higher loading. To avoid exposure of the developed resist to the pure, high pH carbonate/caustic replenishment stream, it has become customary to use carbonate only for the initial developer make-up, and use the carbonate/caustic mix for replenishment only.

The question arises how high a loading is acceptable before the quality of the developed resist image suffers? We did some scouting to obtain that information (Ref. 3). A laboratory "beaker test" with a commercial aqueous dry film plating resist suggests that at more than three times "normal" loadings, time-to-clean did not increase, provided that pH of the potassium carbonate-based developer was held constant by KOH addition: the development speed of resist in fresh potassium carbonate solution was measured. The solution was then loaded with 36 mil-sqft/gal of resist instead of the customary <12 mil-sqft/gal. Then KOH was added until the pH of the solution increased to its original value. The time-to-clean in such a solution was then measured, compared to the original time-to-clean, and found to be the same.

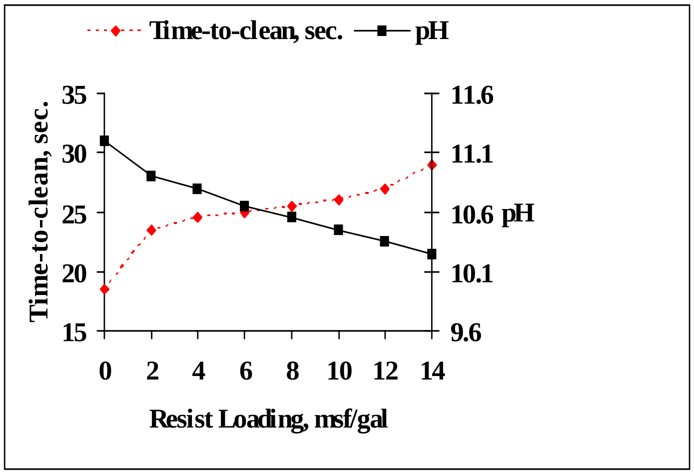

Figure 2: Development Time and pH vs Loading

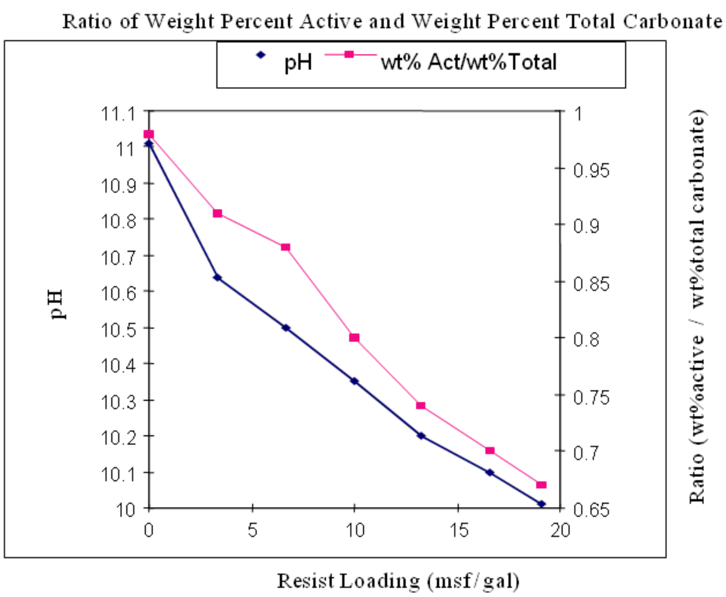

Figure 3: Ratio of wt% Active and wt% Total Carbonate

A loading test up to 30 mil-sqft/gal in a conveyorized (Chemcut CS2000) spray developer gave similar results. We should however keep in mind that time is a factor that will influence results: if we let a developer solution, loaded to 36 mil-sqft/gal, sit for 24 hours, time-to-clean will probably increase greatly because active carbonate will be consumed in a secondary reaction through the saponification of ester groups in the developed resist.

One should of course also verify that other performance parameters are not adversely affected, such as the quality of the developed resist sidewall, the cleanliness of the copper at the bottom of the developed resist channel, and the propensity of the loaded resist solution to “sludge out”. To obtain the most meaningful information regarding these important performance parameters, such tests should be conducted for each resist since the resist formulation will influence the result. In the case of our particular test resist, the developed resist image quality as judged by SEMs did not suffer as resist loading increased and as KOH was added to bring the pH back up to the original value. However, our test resist was known for its good development latitude, and it would be prudent to run similar tests for each resist.

References

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