THE EFFECT OF OPERATIONAL MODE ON PARTICLE CONCENTRATIONS IN BULK CHEMICAL DELIVERY SYSTEMS

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BIBLIOGRAPHY

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ABSTRACT

Bulk chemical delivery systems can be made to deliver chemicals with low particle concentrations. However, the particle levels in the chemicals delivered is highly dependent upon how the system is designed and operated. This paper discusses how system design and mode of operation can be optimized to obtain low particle levels.

INTRODUCTION

The processes used to manufacture state-of-the-art semiconductor circuits presently require the use of numerous liquid chemical reagents. These fluids tend to contain high concentrations of particles which cause process problems. Hence, the industry is attempting to eliminate all processes which require use of liquid reagents and replace them with dry processes. However, replacement processes are slow in coming, and it appears that it will be at least 10 to 15 years before the need for liquid chemicals is greatly reduced.

During the next 10 to 15 years the complexity of the semiconductor devices that are developed will continue to increase and they will be more sensitive to contamination. It will be necessary for chemical quality to continuously be improved if these devices are to be manufactured with a reasonable yield. Improvements will be needed in both dissolved and particulate contamination [1].

The dissolved contaminants in semiconductor process chemicals are mainly controlled by the chemical supplier although some manufacturing facilities include chemical reprocessing systems to increase chemical purity. On the other hand, particulate contaminants in these chemicals are dependent upon and can be controlled by the method in which the chemicals are packaged and supplied to the points of use (POUs) [2].

Tonti [3] has shown that chemical cleanliness requirements will increase significantly over the next several years with particle specifications decreasing by a factor of ten every 3 to 5 years as shown in Figure 1. Hence, particle control in chemicals needs to be continuously improved for the next 10 years or more.

Chemicals can be delivered to the POUs in bottles or by chemical delivery systems. Chemical delivery systems have been shown to supply chemicals with particle concentrations well below those delivered in bottles [4,5]. However, the concentrations of particles in the chemicals delivered by these systems are highly dependent upon the system mode of operation and the type of chemical being delivered. This paper discusses how the operational mode can be optimized so that low particle chemicals can be delivered.

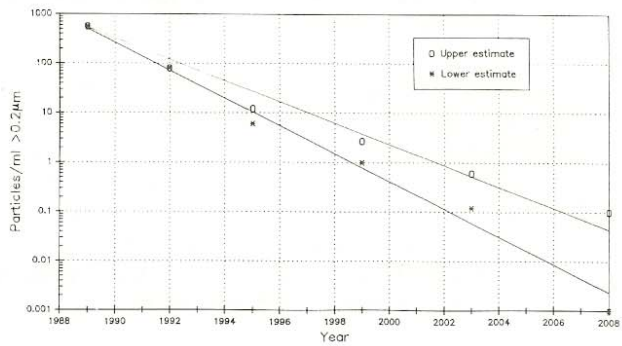

Figure 1: Projected Ultrapure Chemical Particle Purity Requirements (Based on Tonti, Swiss Contamination Control 3(4a):384-387(1990)

BACKGROUND

Previous studies have shown that the flow of chemicals through filters in chemical delivery systems must be maintained at all times in order to achieve low particle levels [4]. If not, particle levels spike each time flow is started and slowly decrease as flow is continued. Also, changes in flow rate were shown to result in particle level increases, especially changes from high to low flow rate.

An example of this type of behavior is shown in Figure 2. This figure presents particle concentrations measured in ammonium hydroxide during a simulated chemical demand cycle. The simulated demand cycle was one hour in duration and is described in Figure 2. The cycle was repeated 8 times in this test. The data indicate that particle concentrations decreased dramatically during continuous high flow demand periods and when flow through the filter was increased. However, particle concentrations increased whenever flow was started or decreased.

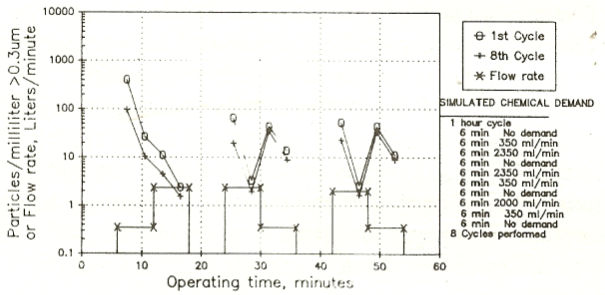

Figure 2: The Effect of Filter Flow Rate Changes on Ammonium Hydroxide Particle Concentrations (from Reference 4)

In addition, the spikes in particle concentration were reduced by continuously recirculating fluid through the system thus preventing stoppage of flow through the filter. This mode of operation has been termed **stabilized filtration**. An example of the use of stabilized filtration to control particle levels in ammonium hydroxide is shown in Figure 3 [4]. As indicated, particle concentrations were greatly reduced and more stable.

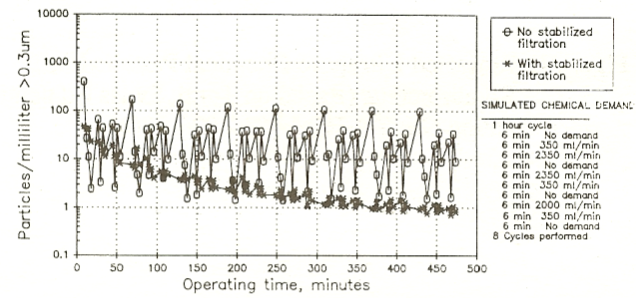

Figure 3: The Effect of Stabilized Filtration on Ammonium Hydroxide Particle Concentrations (from Reference 4)

Stabilized filtration was found to be effective in reducing particle levels in each of four chemicals tested: 37% hydrochloric acid, 30% hydrogen peroxide, 29% ammonium hydroxide and 96% sulfuric acid. However, the particle levels in the various chemicals were vastly different as shown in Figure 4. Particle levels in sulfuric acid were approximately 1000 times those measured in hydrochloric acid with intermediate concentrations measured in ammonium hydroxide and hydrogen peroxide. The reason(s) for the differences is unknown.

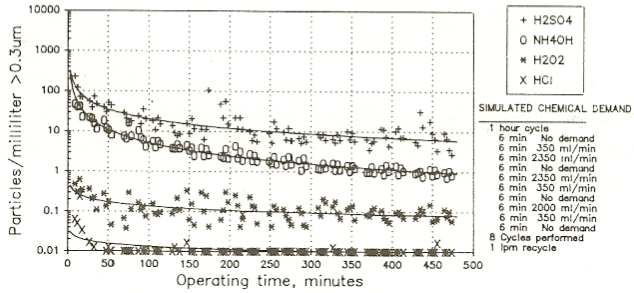

Figure 4: The Effect of Chemical Type on Particle Concentrations (from Reference 4)

It was also found that the majority of the particles in the distribution system during stabilized filtration did not pass through the system filter but rather originated downstream of the filter[4]. This was not unexpected since a 0.3µm optical particle counter (OPC) was used to measure the performance of 0.2µm filters. The particle source was shown to be downstream of the filters by performing experiments in which the distribution system was operated for many hours in a total recycle mode to yield low particle concentrations in both the feed and filtrate. The feed was then switched to one containing approximately 100 times more particles. When this was done using hydrogen peroxide, no change in particle level was seen. A slight increase (20-50%) was seen in sulfuric acid. If the source of the particles downstream of the filter was the incoming particles, one would expect a 100 fold increase in the particle concentration downstream of the filter when the feed change was made.

TESTING OBJECTIVES

The results described above led to this study which is a joint effort between Ashland Chemical, Inc. and FSI International, Inc. The objective of the study is to better define and optimize the variables which control particle concentrations in chemical delivery systems. The study is being performed using sulfuric acid since the previous study indicated that it was the most difficult chemical in which to obtain low particle levels [4]. To date, experiments have concentrated on eliminating the particle spikes which occur during flow interruptions. Two modes of operation have been examined in an attempt to eliminate the spikes:

- Delivery module stabilized filtration
- Fab-wide stabilized filtration

Simplified flow schematics for these modes of operation are compared to a single pass filtration mode in Figure 5. In single pass filtration the chemical to be delivered is transferred from a supply drum to a receiver using a positive displacement pump. The receiver is pressurized with process quality nitrogen to pass the chemical through filters and deliver it to the fab. In delivery module stabilized filtration, stabilized filtration is incorporated within the system delivery module. The delivery module includes the feed supply drum (or tank), pumping system, receiver and filters. In fab-wide stabilized filtration, stabilized filtration is achieved by recirculating chemical through the loop supplying chemical to the wafer processing equipment.

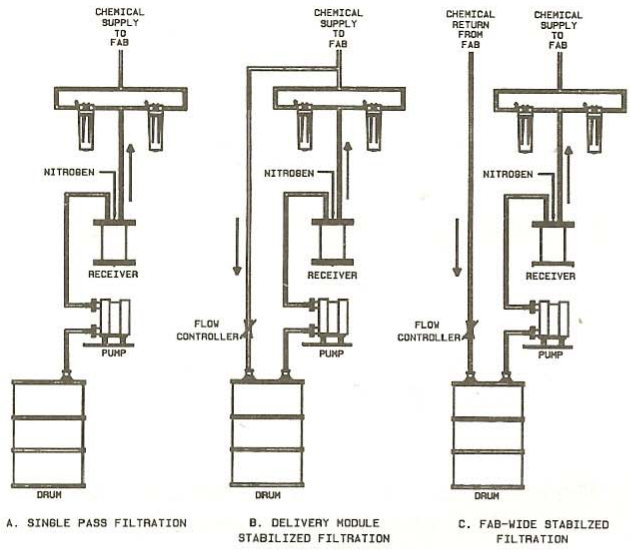

Figure 5: Operational Mode Simplified Flow Schematics

A flow schematic of the test system used to evaluate the modes of operation is shown in Figure 6. The system includes a delivery module and all of the filters, plumbing and valving required to perform the modes of operation described above. The filters used in these tests were PF-80 stacked-disc cartridges (Millipore Corporation, Bedford, Massachusetts) containing 0.2µm PTFE filter media. All of the wetted parts in the system are Teflon® PFA or PTFE. The system also includes three particle sensors and a distribution loop supplying chemical to a simulated fab. The distribution loop consists of 250 feet of 3/4 inch OD Teflon PFA tubing and two POUs. The POUs each consist of a pneumatically controlled valve and a flow controller. The flow controllers are set to deliver 350 and 2000 ml/min, respectively. Chemical supplied by the POUs go to an external drum.

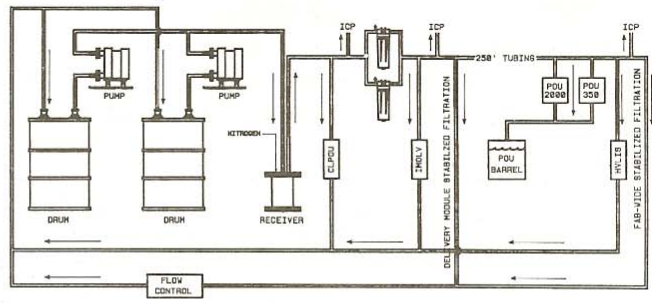

Figure 6: Test System Simplified Schematic

The three particle sensors included in the system were manufactured by PMS (Boulder, Colorado). All are OPCs with different operating characteristics. Two of the sensors, an HVLIS and an IMOLV, were used to measure filtrate particle concentrations. A third, a CLPOU was used to measure the concentration downstream of the receiver and upstream of the filter. The three sensors were operated using the following conditions:

Sensor	Sensor Type	Flow Rate ml/min	Sensed Flow ml/min	Minimum Size Detected, µm
HVLIS	In-situ	300	15	0.2
IMOLV	Volumetric	25	25	0.3
CLPOU	In-situ	1000	0.5	0.2

Prior to performing the experiments in this study the HVLIS and IMOLV sensors were compared using water and sulfuric acid. The two counters detected similar concentrations of particles >0.3µm in DI water. However, in sulfuric acid the concentrations of particles >0.3µm measured by the HVLIS were 2 to 10 times those indicated by the IMOLV. The discrepancy is thought to result from differences between the optical components in the two instruments. Because of this discrepancy, direct comparisons of particle concentrations measured by the two instruments cannot be made.

The HVLIS was placed at the end of the loop since it was the most sensitive instrument and required a flow of only 300 ml/min. The IMOLV was used to measure the particle concentration immediately downstream of the filter because of its low flow requirement. The CLPOU was used to measure the concentration upstream of the filter because of its high flow requirement and relatively high background counting rate.

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OPERATIONAL MODE COMPARISON

Figure 7 shows particle concentrations measured immediately **downstream of the system filter** when the system was operated using the following simulated demand cycle:

Operating Time Minutes	Operating Time Hours	Chemical demand, ml/min
0 - 240	0.00 - 4.00	0
240 - 245	4.00 - 4.08	350
245 - 250	4.08 - 4.17	0
250 - 255	4.17 - 4.25	2000
255 - 260	4.25 - 4.33	2350
260 - 280	4.33 - 4.67	0
280 - 285	4.67 - 4.75	350
285 - 290	4.75 - 4.83	0
290 - 300	4.83 - 5.00	2000
300 - 330	5.00 - 5.50	0
330 - 335	5.50 - 5.58	2350
335 - 345	5.58 - 5.75	0
345 - 350	5.75 - 5.83	2000
350 - 355	5.83 - 5.92	0
355 - 360	5.92 - 6.00	2000

This cycle was repeated one or two times in all experiments.

Two curves are shown in Figure 7, one for each of the operational modes evaluated. Similar curves are shown in Figure 8 for particle concentrations measured at the **end of the distribution loop**. Each of the curves shown in Figures 7 and 8 represent the average of 3 to 5 runs. Note that Figure 7 describes the concentration of particles >0.3μm measured with the IMOLV sensor while Figure 8 is for particles >0.2μm measured using the HVLIS sensor. Also, recall that the HVLIS indicated higher concentrations of particles than the IMOLV.

Since particle levels obtained in delivery systems without stabilized distribution are typically ≥100/ml [4], Figure 7 indicates that stabilized filtration reduced the number of particles immediately downstream of the filter by more than two orders of magnitude. Particle concentrations were seen to continuously decrease for four hours, increase slightly (several particles per milliliter) for two hours, decrease for four hours then increase slightly. The periods in which the concentrations decreased correspond to times when there was no POU activity. The increases occurred when the POUs were active and are probably a result of changes in the flow rate of chemical through the filter. The changes in particle concentration were much smaller than when stabilized filtration was not used. Similar results were obtained with delivery module and fab-wide stabilized filtration.

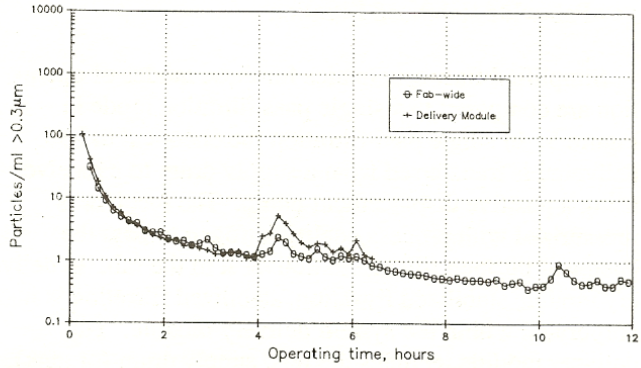

Figure 7: The Effect of Filter Stabilization Mode on Particle Concentrations at the Delivery Module Filter Outlet

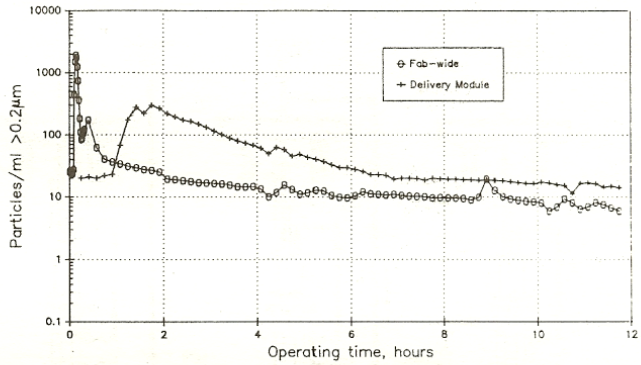

Figure 8: The Effect of Filter Stabilization Mode on Particle Concentrations at the End of the Distribution Loop

Figure 8 indicates that particle levels at the end of the distribution loop were strongly influenced by the stabilization mode. In both modes of operation the particle concentrations were initially low, increased significantly, then decreased towards the initial levels. When fab-wide stabilized filtration was used the increase occurred sooner, resulted in a higher concentration and recovered more quickly than when delivery module stabilized filtration was used.

Figure 9 shows that the increase in particle concentrations occurred about 5 minutes after the test was started when fab-wide stabilized filtration was used and one hour after the test was started when delivery module stabilized filtration was used. The times for the increase to occur correspond to the times required to displace the clean chemical remaining in the distribution loop from the previous test with the chemical exiting the filter housing. Hence, it was concluded that the increase in particle levels occurred as a result of stopping and starting flow through the filter. The reason for the increase is presently under investigation.

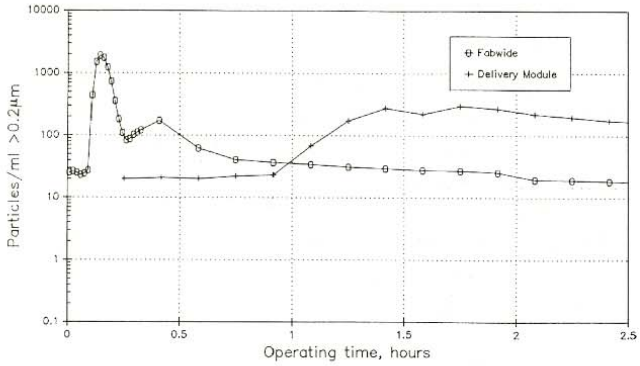

Figure 9: The Effect of Filter Stabilization Mode on Particle Concentrations at the End of the Distribution Loop

The peak in concentration seen with fab-wide filter stabilization is thought to be higher than the one obtained using delivery module stabilization for two reasons. First, all of the particles "generated" when the flow through the filter was interrupted were sent through the distribution loop in fab-wide stabilization while only a fraction of them entered the loop when delivery module stabilization was used. Only a fraction of the particles entered the distribution loop during delivery module stabilized filtration because the majority of the flow in the system was recirculated around the delivery module. The only fluid entering the distribution loop was that demanded by the POUs and the HVLIS particle counter. The other reason that the peak occurring in delivery module stabilized filtration was smaller is that the higher flow rate and resulting decreased residence time in the distribution loop during fab-wide stabilized filtration resulted in less mixing in the loop. The increased mixing which occurred during delivery module stabilized filtration resulted in a shallower, broader peak. The slower recovery of particle concentrations which occurred during delivery module stabilized filtration is also due to the lower flow through the distribution loop.

Figures 8 and 9 indicate that even when stabilized filtration is used, it takes time for filter stabilization to be effective. Also, the particles in the chemical during the peaks are larger than those in the chemical once stabilization has significantly reduced particle levels. This is shown in Figure 10 which presents particle size distributions measured after stabilization was effective (termed steady state) and during the peaks which occurred during the two stabilization modes. As shown, the peaks contained larger fractions of large particles.

Since both modes of filter stabilization described above resulted in increased particle concentrations entering the distribution system upon startup, a third mode of stabilization was examined. This mode incorporated delivery module filter stabilization and a short (less than 1 hour) delay time before chemical was allowed to pass into the distribution loop. In this way particles "generated" when the flow through the filter was interrupted could be removed before the chemical was dispensed to the POUs. Also, since it is only necessary to utilize this delay time when chemicals drums or filters are changed, it will not significantly reduce the productivity of the delivery system.

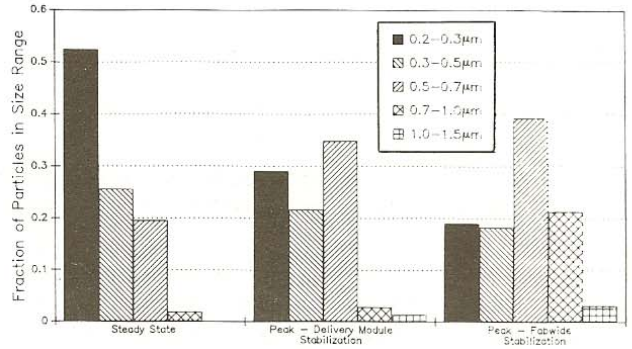

Figure 10: Comparison of Particle Size Distributions During Concentration Peaks and Steady State Operation

The use of a delay time virtually eliminated the increase in particle concentrations in the distribution loop as shown in Figure 11. Hence, this mode of operation was shown to yield the lowest particle concentrations.

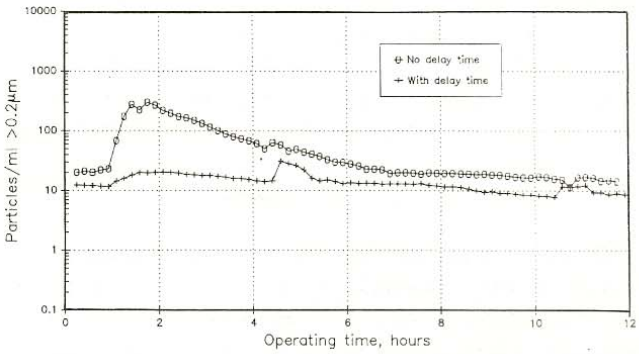

Figure 11: The Effect of Incorporating a Delay Time with Delivery Module Stabilization on Particle Concentrations at the End of the Distribution Loop

FUTURE ISSUES

Figure 11 indicates that by optimization of the system mode of operation low concentrations of particles >0.2µm can be achieved. However, recent measurements using a PMS M65 sensor, which detects particles >0.065µm in diameter, indicate that these chemicals contain large numbers of smaller particles. Measurements were made immediately downstream of the delivery module filter in hydrochloric acid and sulfuric acid after 45 minutes of filter stabilization. The particle size distributions measured are shown in Figure 12. They indicate that additional system optimization is required to achieve low concentrations of smaller particles.

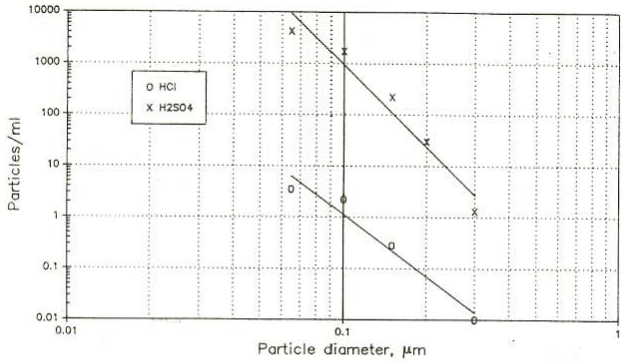

Figure 12: Particle Size Distribution Measured in Two Acids after 45 Minutes of Filter Stabilization

Another concern is the source of the particles generated when the flow through the filter is stopped. Are the particles shed from the filter? Are they particles which were removed from the fluid by the filter and then released when the flow through the filter is stopped and restarted? Are they shed from the filter housing and tubing, etc.? Are they from some other source? If the source of the particles can be identified perhaps it can be eliminated and system design can be further optimized.

Another area of concern is the reason for the different particle levels in different chemicals (Figure 4). Are these differences due to particle counting methodology? Are they a result of particle shedding or chemical degradation? Chemical degradation is a possibility as Teflon has been shown to release particles in some chemicals[6].

CONCLUSIONS

The concentrations of particles in chemicals supplied by bulk delivery systems is highly dependent upon the way in which the system is designed and operated. In particular, it is important to maintain flow through filters used in the systems at all times in order to obtain low particle concentrations. This mode of operation, termed stabilized filtration, prevents the "generation" of large numbers of particles which occurs whenever the flow through the filters is stopped and restarted.

When systems do not have stabilized filtration, particles "generated" upon stopping and starting flow through the filters must be prevented from reaching the points of use. This can be achieved by re-establishing filter stabilization prior to dispensing the chemical to the points of use.

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