SEMICONDUCTOR INDUSTRY FILTRATION SOLUTIONS FOR 300 MM HIGH-FLOW AND HIGHER-VISCOSITY RECIRCULATED APPLICATIONS

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Introduction

Liquid filtration has been used in the manufacturing of semiconductor devices for many years. Many of the processes use wet bench style equipment which incorporates both contamination control and pumping in the form of chemical filters and chemical pumps. These wet benches are typically in the form of recirculated baths which use filtration, pumps and other piping equipment.

Due to increasing contamination control requirements, it is critically important to upgrade the filtration to smaller pore size ratings. It has been well established that smaller pore size (tighter) rated filtration will result in increased pressure drop and resistance across the filter. As a result, the move towards tighter filtration will have an effect on the flowrate in a recirculated bath system. The purpose of this application note is to understand the effects on system flowrates when moving to tighter filtration for applications with various flowrates.

Importance of Retention and Flowrate

Historically, filters with high flowrate would sacrifice in their particle removal capability known as retention. However, future semiconductor device will require both higher flowrate without a sacrifice in retention.

Bath Particle Cleanup Equation

The particle performance in a recirculated bath can be described as being a function of flowrate through the bath particle removal efficiency of the filter. It can be assumed that the bath behaves as a continuous stirred tank reactor (CSTR). As the clean chemical enters the bottom of the bath, it mixes with the dirty chemical in the bath. As the filter removes particles continuously, the particle level in the bath will decrease in an exponential form. The decrease in the particle concentration in the bath can be modeled using Equation 1. Figure 1 provides a schematic of a typical recirculated bath[1].

$$C = C_0 e^{-QRt/V} \quad (1)$$

where

C = particle level in the bath (particles/ml) at any time (t)

C_0 = initial particle level in the bath (particles/ml)

Q = flowrate through the bath (l/min.)

R = fractional retention of the filter

V = volume of the bath (liters)

Based on this model, both higher flow rates and higher retention will lead to faster bath cleanup.

Typically, a filter with very high flowrate will not have as high retention and filters with high retention will have a low flowrate. Ideally, a filter with both high flowrate and high retention would yield the best bath cleanup results. For example, Table 1 lists how the model would predict the bath cleanup for filters of various flowrate and retention properties.

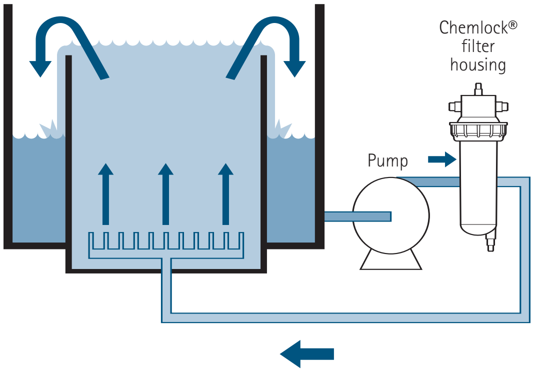

Figure 1. Simple diagram of a recirculating chemical bath

PREDICTED BATH CLEANUP FOR VARIOUS FILTERS

QuickChange® Filter	Membrane Area (m²)	Flow Rate* (l/min.)	PSL Retention for 0.03 µm Particles (LRV)	Time to Remove 99% of Particles in Bath (min)**
0.1 µm ATX	1.3	17	0.7	11.8
0.03 µm ATM	1.8	10	3.5	9.9
0.03 µm ATE	2.2	17	3.5	9.4

* *Flowrate at constant pressure of 20 kPa for DI water @ 25°C*

** *EJ-90 model pump; 43 PSIG operating pressure; 20 l/min. flowrate w/o filter; 1.7 cP; 1 g/cm³ fluid*

Table 1. Predicted bath cleanup for various filters

Therefore, it is important to understand what factors affect the flowrate of a system which in combination with the particle removal capability of the filter will determine the recirculated bath particle cleanup.

Pressure Losses in a Recirculating Bath Application

Let us begin by understanding the source of pressure losses in a typical recirculated application. The total resistance in a recirculated bath system can affect the flowrate in the bath. This total resistance can be divided into three contributions[2]. These include pressure losses due to the filter, piping and hydrostatic head.

Filter Resistance

The pressure losses due to the filter are considered to be laminar flow losses. These losses can be modeled as flow through a pipe using the Hagen-Poiseuille equation. In this equation the pressure drop is proportional to the flowrate and viscosity to the first power[3].

The filter resistance is most easily measured with a water pressure drop test using during the manufacturing of the filter. Smaller pore size ratings of the filter will result in higher resistances or lower flowrates. Table 2 lists an example of decreasing pore size rated filters and their respective resistances and flowrates.

RESISTANCE OF SEVERAL ENTEGRIS LIQUID CHEMICAL FILTERS

Pore Size Rating (µm)	Resistance (PSID/GPM-cP)	Flow Rate* (l/min.)
0.1	0.45	27
0.05	0.65	19
0.03	1.2	10

* *Flowrate is at 25°C; 20 kPa pressure*

Table 2. Resistance of several Entegris liquid chemical filters

Piping Resistance

The pressure losses due to piping are generally turbulent flow losses. These losses can be modeled as flow through a pipe using the Bernoulli equation[4]. In this equation the pressure drop is proportional to the flowrate squared and density to the first power.[5] Note that these losses are independent of the viscosity (µ) of the process fluid.

Hydrostatic Head Resistance

The third contributor is the hydrostatic head which is related to the height of the chemical required to overflow the weir. This element is independent of flowrate and is usually insignificant of typical recirculated baths. Therefore, this contribution will be neglected in the following calculations.

Total Resistance

Therefore the total resistance of the filter can be calculated by the sum of the filter and piping resistance.

Understanding Pump Curves for Achieving Flowrate Requirements

A chemical pump needs to generate the pressure and flow that will pass through the filter and piping. As the pressure drop of the filter increases, the system moves up the pump curve resulting in the pump generating more pressure and less flowrate. Note that some of the factors which can result in an increase in the filter's pressure drop include plugging, dewetting, inefficient venting or a combination of these factors.

Reciprocating pumps are a form of pumps commonly used in the microelectronic industry. Air-operated bellows or diaphragm pumps are two examples of such pumps. These pumps can be operated at various air pressures resulting in varying pump curves. Figure 2 provides an example of the pump curves for an Entegris EJ-90 model air-operated bellows pump.

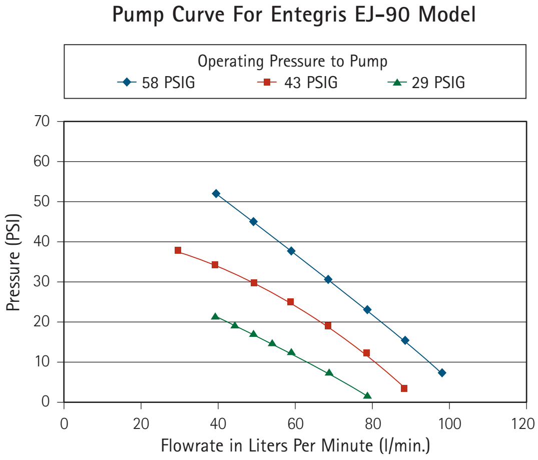

Figure 2. Air-operated bellows pump Entegris EJ-90 model

Such pump curves can be fit to second order polynomials with unsolved coefficients.

Therefore, for a given set of conditions of filter and piping resistance, a known value of density and viscosity, the flowrate in a bath can be calculated. In summary, for a given pump curve and filter combination, there is a single flowrate under which the recirculating bath will operate.

Model Calculation Examples:

Consider the following set of conditions for 50 nm rated QuickChange® ATM filter.

- EJ-90 model air-operated bellows pump @ 43 PSIG
- Filter resistance = 0.65 PSID/GPM-cP
- Viscosity = 1 cP
- Density = 1 g/cm³
- Flow of system with no filter = 9 GPM

Under these assumptions the system flowrate would be calculated to be 32 l/min.

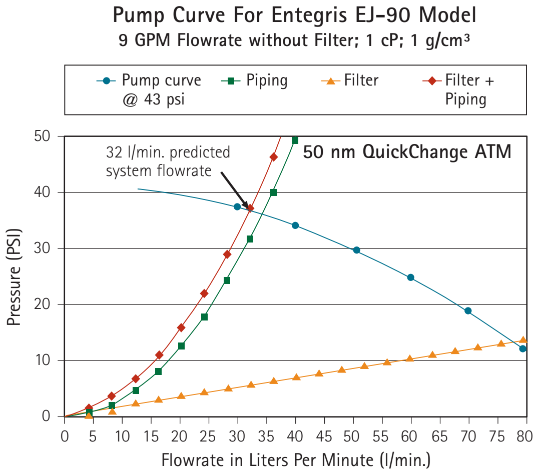

Figure 3. Predicted flowrate 50 nm QuickChange ATM filter at 1 cP

Now consider the set of conditions in which a 30 nm QuickChange ATM filter is used. In this case the filter has a smaller pore size rating and will result in higher pressure drop.

- EJ-90 model air-operated bellows pump @ 43 PSIG
- Filter resistance = 1.2 PSID/GPM-cP
- Viscosity = 1 cP
- Density = 1 g/cm³
- Flow of system with no filter = 9 GPM

Under these assumptions the system flowrate would be calculated to be 30 l/min.

In this case, there would only be a 2 l/min. drop (~6%) in flowrate when upgrading the filtration in the system from a standard 50 nm ATM to a standard 30 nm ATM filter. These would be the results for a fluid with a viscosity of 1 cP. Figure 4 provides a graphical solution of these results.

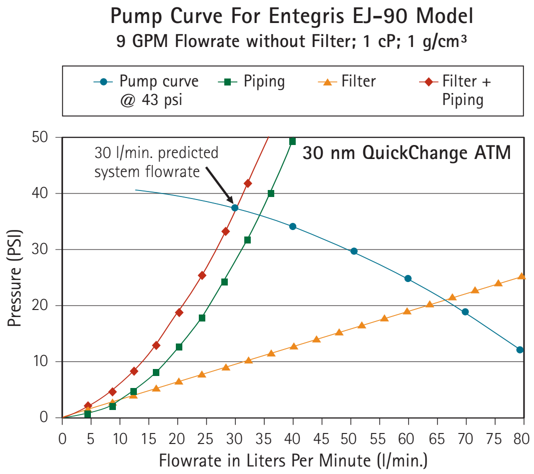

Figure 4. Predicted flowrate 30 nm QuickChange ATM filter at 1 cP

Effects of Fluid Viscosity on System Flowrate

The model calculations were performed for set of varying viscosities and a given density of 1 g/cm³. The calculation was done for two filters using the same bellows pump. The two filters were an open and tight filter with resistances of 0.72 and 1.2 PSID/GPM-cP, respectively.

The results show the effects on switching from a 30 nm QuickChange ATM filter to a filter with the same pore size rating but with less resistance. This filter is known as the 30 nm QuickChange ATE filter which has been designed to increase its flowrate. Moving from the ATM filter to the higher-flowing ATE resulted in about 5% increase in system flowrate for the 1 cP condition. However, as the fluid viscosity increases to 1.5, 1.7, 1.9 and 3.5 cP, the bath flowrate increased by 7.5, 8.5, 9.5 and 18% respectively when using the ATE filter. Therefore, the effects of the tighter filter are much more significant for the higher viscosity fluids. Figure 5 provides a summary of the results.

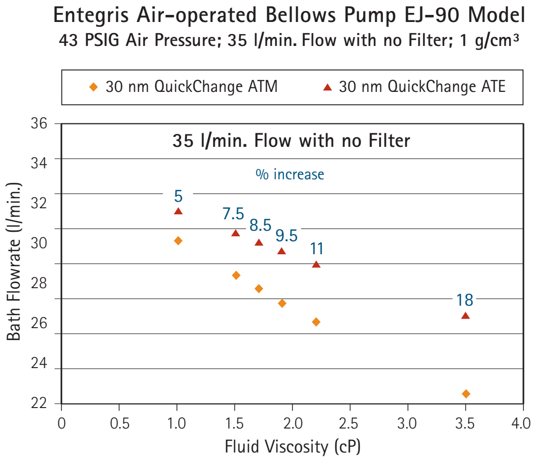

Figure 5. Effects of fluid viscosity on system flowrate for 30 nm ATM vs. 30 nm ATE filters for 35 l/min. without filter

Effects of Piping Resistance

The calculations so far have been made for conditions when 35 l/min. is the flow rate of the system with no filter. This range of flowrate is considered higher compared to traditional 200 mm wafer processes but is applicable for some 300 mm processes.

Let us consider the set of conditions in which the flowrate of the system with no filter is 20 l/min. Recalculating the bath flowrates comparing a 30 nm QuickChange ATM and 30 nm QuickChange ATE filter yields different results. Now the piping resistance has more effect on bath flowrate and flowrate increase when moving from ATM to ATE is not as significant. Figure 6 provides a summary of the results.

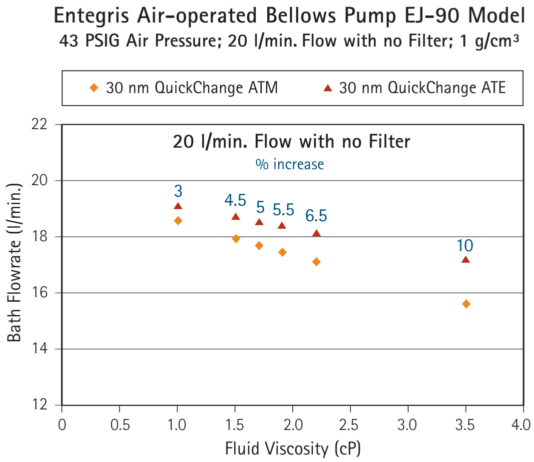

Figure 6. Effects of fluid viscosity on system flowrate for 30 nm ATM vs. 30 nm ATE filters for 20 l/min. without filter

So when the piping resistance is larger as in the case of applications that run at 20 l/min. without a filter, the benefit in flow improvement is not as significant. However, 300 mm wafer processing applications which run at higher flowrates can see the significant increase in bath flowrate when using higher-flowing filters. Figure 7 provides a summary of the effects of bath flowrate without a filter when switching from a 30 nm QuickChange ATM to a 30 nm QuickChange ATE filter.

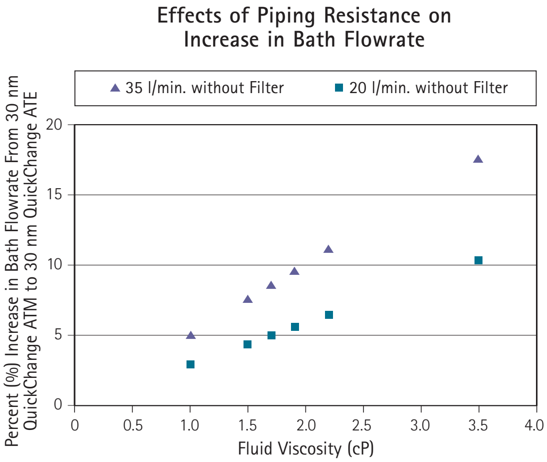

Figure 7. Effects of piping resistance on system flowrate when moving to higher-flowing filters

Customer Results vs. Bath Model Predictions

The data shown so far are bath flowrate predictions based on the previously mentioned model. In order to verify the accuracy to which the model predicts bath flowrates in a real application, filters were tested at a customer to test the various effects of bath flowrate.

Experimental Setup

The evaluation at the customer was done on a recirculated bath system designed for 300 mm wafer processing. The chemical used was sulfuric acid and the pump type was an Entegris EJ-90 model chemical bellows pump. The bath was approximately 13 gallons in volume. The application used an in-line heater for heating the chemical. A pressure transducer and flow monitor was used to measure the pressure drop and flowrate through the filter during the experiment. Figure 8 provides a schematic of the experimental test setup.

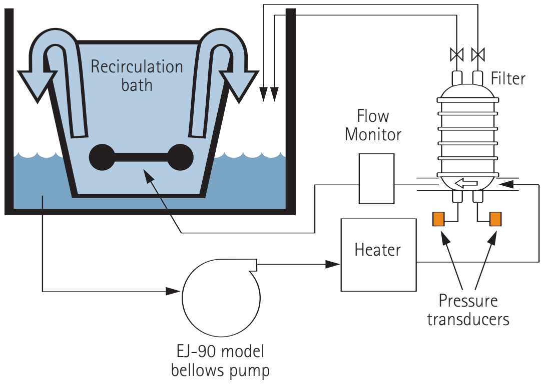

Figure 8. Experimental setup at customer

Experimental Conditions

VISCOSITY AND TEMPERATURE

The temperature of the chemical bath system was varied from 80 to 140°C. The varying temperature conditions resulted in the sulfuric acid changing in viscosity. Table 3 shows a summary of the viscosity of concentrated sulfuric acid as a function of temperature.

EFFECTS OF TEMPERATURE ON SULFURIC ACID VISCOSITY

98% Sulfuric Acid Temperature (°C)	 Viscosity (cP)
25	17.0
80	3.5
110	2.2
120	1.9
130	1.7
140	1.5

Table 3. Effects of temperature on sulfuric acid viscosity

FILTER RESISTANCE

An example of two filters with varying flow resistances were used for the evaluation. These filters are the Entegris 30 nm QuickChange ATM and 30 nm QuickChange ATE. The QuickChange ATE product has been designed so that it has less resistance but does not sacrifice in its 30 nm particle removal capability. Table 4 lists a summary of the resistance of the filters mentioned:

FILTER RESISTANCES FOR 30 NM PRODUCTS

Filter	ΔP @ 1 GPM* (PSID)	Flowrate @ 20 kPa** (l/min.)
30 nm QuickChange ATM	1.2	10
30 nm QuickChange ATE	0.72	17

** DI water @ 1 cP ** DI water @ 25°C*

Table 4. Effects of filter resistances for 30 nm products

PIPING RESISTANCE

The piping resistance of most systems can be measured by measuring the flowrate in the system with no filter in place. This value can vary with by changing the operating pressure to the pump. This value can also change by varying the temperature of the chemical in the bath.

Using the following assumptions, the model was used to predict the calculated bath flowrate the following conditions for an EJ-90 model bellows chemical pump.

ASSUMPTIONS AND CONDITIONS FOR BATH FLOWRATE CALCULATIONS

Filter	Sulfuric Acid Temperature (°C)	 Viscosity (cP)
ATM vs. ATE	140	1.5
ATM vs. ATE	130	1.7
ATM vs. ATE	120	1.9
ATM vs. ATE	110	2.2
ATM vs. ATE	80	3.5

Table 5. Assumptions and conditions for bath flowrate calculations

The bath flowrate calculations were then compared to the real bath flowrate measured at the customer using the same conditions as above.

The results showed excellent agreement for both the ATM and ATE filters with respect to predicting the bath flowrate. Figures 9 and 10 provide a summary of the calculated vs. the real bath flowrates.

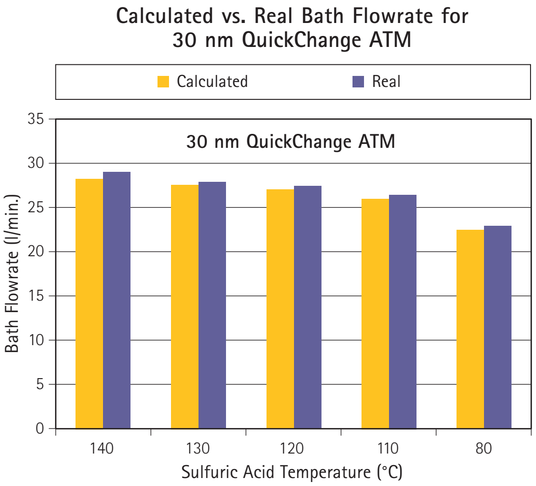

Figure 9. 30 nm QuickChange ATM calculated vs. real flowrate in sulfuric acid bath

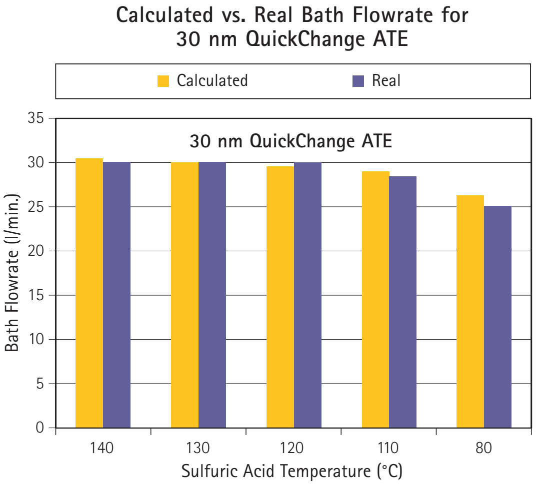

Figure 10. 30 nm QuickChange ATE calculated vs. real flowrate in sulfuric acid bath

Since it has been demonstrated that the bath flowrate can be accurately calculated, we can see the improvement in bath flowrate when moving to a lower resistance filter. Figure 11 provides a summary on the bath flowrate improvement when moving from 30 nm QuickChange ATM to 30 nm QuickChange ATE. Note that as temperature of the sulfuric acid decreases, the viscosity increases and the flowrate effect on moving to the QuickChange ATE product is more significant.

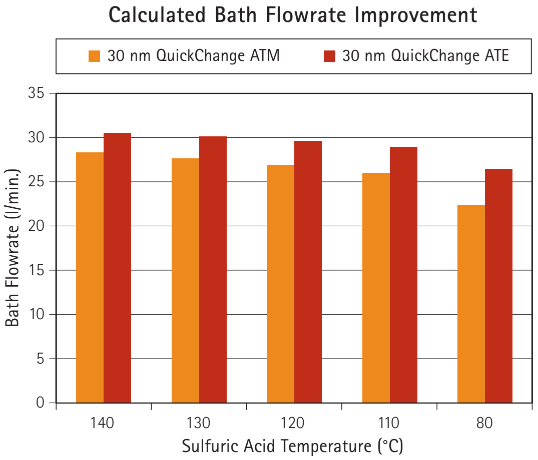

Figure 11. Calculated bath flowrate improvement

Bath Cleanup Model vs. Real Results

Using the previously described bath cleanup model in combination with the bath flowrate model, we can calculate bath cleanup for various conditions. Consider the following set of application conditions.

MODEL CONDITIONS FOR FILTER EVALUATION

Pump Model	Filter	Chemical	Temp. (°C)	Viscosity (cP)	Operating Pressure (kPa)	Bath Flowrate (l./min.)
EJ-90	30 nm QuickChange ATE	SPM	130	1.7	200	24
EJ-90	30 nm QuickChange ATM	SPM	130	1.7	200	21
EJ-90	30 nm QuickChange ATE	H_3PO_4	160	3	200	18

Table 6. Model conditions for filter evaluation

The bath flowrate model predicts that the lower resistance filters such as QuickChange ATE filter will result in higher flowrate in the system compared to a QuickChange ATM for the same rating. The model also predicts that the higher viscosity phosphoric acid test will cause in a decrease in bath flowrate for the same filter. Finally, the bath cleanup model higher system flowrates will cause faster bath particle cleanup.

In summary higher system flowrates will result in faster bath particle cleanup and these flowrates are mainly affected by the filter's pressure drop and the viscosity of the chemicals. Figure 12 provides a summary of the predicted bath cleanup results.

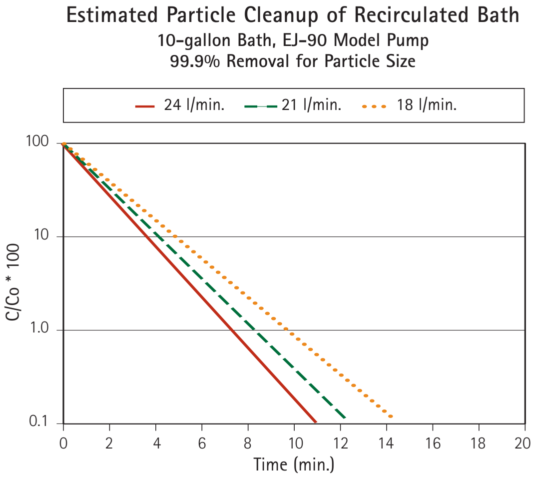

Figure 12. Predicted bath cleanup for 30 nm QuickChange for various flowrates

The filter was tested in a real customer bath in which the particle counts in the bath were measured using a Rion KS17-AF optical particle counter capable of detecting particles down to 0.06 µm in size. Since the filter was the 30 nm QuickChange ATE it can be assumed that the filter has >99.9% retention for particles at 0.06 µm in size.

The data showed that the particle cleanup in the bath improved with increased operating pressure or increase flowrate in the bath. Figure 13 provides a summary of the results of a 30 nm QuickChange ATE in room temperature H_2O with an EJ-90 model chemical bellows pump. This result can predict the particle performance of a 30 nm QuickChange ATE in an 80°C H_2SO_4 application.

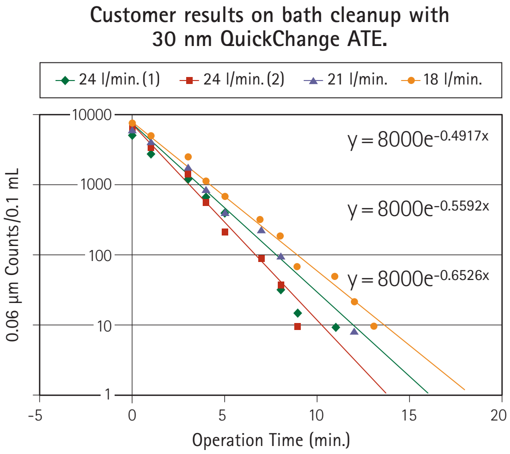

Figure 13. Customer results on bath cleanup with 30 nm QuickChange ATE

The disadvantage of increasing the pressure is that it will exercise the pump more and may result in shorter lifetime of the chemical pump. The Entegris EJ series of chemical pumps have a machined bellows using a proprietary process that eliminates stress concentration areas and contributes to increased cycle life. In addition, the unique check valve design inside the EJ series pump minimizes particle generation and reduces pump pulsation thereby placing less stress on system mechanics. In addition, there may be some safety issues with the plumbing and fittings which have maximum operating temperatures and pressures.

Physical Properties of Chemicals in Typical Recirculated Baths

The chemicals typically used in recirculated baths for wet processes can be generally summarized into a finite list. Table 7 summarizes the list of typical chemicals for recirculated processes. It can be seen that the ammonium fluoride, sulfuric acid and the organic photoresist stripper example have higher viscosities. These are just a few examples of where moving to tighter filtration may cause flowrate decreases[6].

Please note that some values are estimates based on the contribution of each chemical to mixture.

VISCOSITY AND DENSITY OF TYPICAL CHEMICALS IN RECIRCULATED BATHS

Chemical	Temp. (°C)	Viscosity (µ)	Density (g/cm^3)
Dilute HF	25	1	1
40% NH_4F	25	4	1.3
80% Sulfuric Acid	120	2	1.6
	140	1.5	1.6
SC1	25	1	1.1
	80	0.5	1
SC2	60	0.5	1
Organic Photoresist Stripper A	25	7	1
	45	5.5	1
85% Phosphoric Acid	160	3	1.6

Table 7. Viscosity and density of typical chemicals in recirculated baths

Efficient Venting of Filter Housing

Filters which are hydrophilic or “water-loving” have membranes which will not allow undissolved gas bubbles to pass through it. It can therefore gas lock if the venting is not efficient. By gas locking, the gas builds up on the upstream side of the filter housing and becomes a barrier for the liquid chemical to pass through. This results in increased pressure drop and subsequent loss in system flowrate. Therefore, it is important for the filters to be efficiently vented on startup and periodically in the gas of outgassing applications. Some applications which are especially outgassing incorporate a continuous vent back to the bath.

Recommendations

1. It is important to vent the housing for outgassing applications. This eliminates a pressure drop due to gas-locking that provides no benefit to the system.
2. Use a computer program like the one provided by Entegris to analyze the tool and application to understand what factors control the flow in the system.
3. If higher flow is desired in the system with a high-viscosity chemical, use a higher-area filter. Generally this method requires no modification of the system.
4. If the system can be modified, place two filters in parallel to reduce the effect filter resistance by a factor of two.
5. If no modification in the system can be made, increasing the discharge pressure of the pump can increase the flow in the bath, although there may be a reduction in pump lifetime.

References

1. Zahka, J.G.; Shyu, Jieh Hwa. “Predicting ParticlePerformance in a Recirculated Chemical Bath,” *Entegris Application Note MA059.*
2. Zahka, J.G.; Shyu, Jieh Hwa. “Predicting Particle Performance in a Recirculated Chemical Bath,” *Entegris Application Note MA059.*
3. McCabe, Warren L.; Smith, Julian C.; Harriott, Peter. “Unit Operations of Chemical Engineering,” *Fifth Edition.*
4. McCabe, Warren L.; Smith, Julian C.; Harriott, Peter. “Unit Operations of Chemical Engineering,” *Fifth Edition.*
5. McCabe, Warren L.; Smith, Julian C.; Harriott, Peter. “Unit Operations of Chemical Engineering,” *Fifth Edition.*
6. For a more complete list of photoresist stripper viscosities, please refer to *Entegris Application Note MAL 102.*

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