PRACTICAL GUIDE FOR USING TORRENTO™ AND QUICKCHANGE® ATE FILTERS IN OUTGASSING APPLICATIONS

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Introduction

Nondewetting chemical filters provide several benefits when used in chemistries that are common in semiconductor chip fabrication. For example, many chemicals used in the microelectronics industry contain hydrogen peroxide, ammonium hydroxide and hydrochloric acid. These are just a few examples of outgassing chemistries which result in significant bubble formation.

When filtering these chemistries it is important to appropriately use and vent the filter and housing assemblies so as to not negatively impact the wafer processing.

The purpose of this application note is to provide a practical guide and understanding to customers using the newly developed Torrento and QuickChange® ATE product families.

Wettability, Dewettability and Gas-locking

Wettability

Due to the corrosive nature often found with these chemistries, it is required to use highly compatible and temperature resistant polymeric based filters. The use of PTFE[1]-based Teflon® filters has been well established to have good chemical and temperature compatibility in many semiconductor applications which include SC1[2], SC2[3], SPM[4], etc.

The issue with hydrophobic PTFE membranes is that the surface energy of PTFE is too low to allow the membrane to spontaneously wet with chemicals with higher surface tensions.

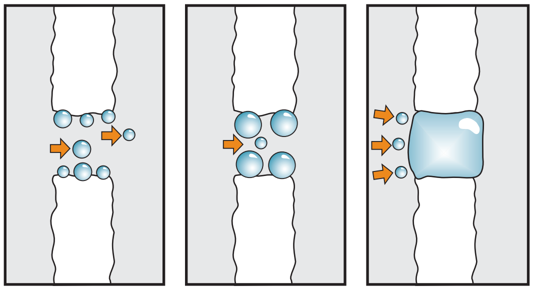
In the past, techniques were used to prewet the PTFE based membrane filters with a low surface tension fluid such as IPA followed by a DI water flush. The filter would then be considered "prewet" and ready for use. Some filter manufacturers already provide "prewet" PTFE filters which are already wet and ready for use out of the box.

Dewettability

Once a membrane is wet with a higher surface tension fluid such as water or sulfuric acid, there are cases in which the pores will tend to dewet. Dewetting is the process by which the liquid inside of the pores will displace out of the pore allow the pore to be filled with gas (Figure 1).

The dewetting phenomenon is more significant for the following conditions:

- Higher surface energy membranes (e.g., PTFE)
- Smaller pore size rated membranes (e.g., 20 nm)
- Outgassing applications (e.g., SC1, SPM)



Hydrophobic PTFE membrane surface energy is 18 dynes/cm; PTFE has a higher affinity for air than water. Gas bubbles stick to the membrane surface, forming nucleation sites.

As more gas bubbles pass through the pore, these nucleation sites grow and begin to block the pore.

Finally, the pore completely fills with gas, effectively blocking the pore and rendering it unusable. As more pores in the filter dewet, the flow through the filter dramatically decreases.

Figure 1. Dewetting on hydrophobic PTFE membrane

About 10 years ago the QuickChange product family was introduced, which consisted of a PTFE-based polymeric membrane with increased membrane surface energy, resulting in a "non-dewetting" membrane (Figure 2).

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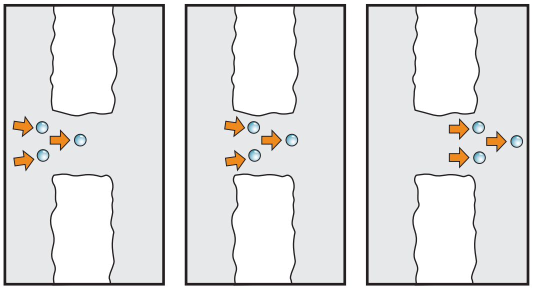
[1] *Polytetrafluoroethylene*

[2] *Mixture of ammonium hydroxide, hydrogen peroxide and water*

[3] *Mixture of hydrochloric acid, hydrogen peroxide and water*

[4] *Mixture of sulfuric acid, hydrogen peroxide and water*



QuickChange membrane surface energy is 35 dynes/cm; when wet, this membrane has a higher affinity for water than air.

Dissolved gas bubbles do not stick to the membrane surface, eliminating the formation of nucleation sites.

Dissolved gas bubbles are swept through the pore, leaving the usable filtration area intact. Flow rates are maintained over extended periods in use.

Figure 2. Nondewetting PTFE membranes maintain their wettability

The product was provided in a prewet condition so that there was no need to prewet with low surface tension fluids. The advantage of the QuickChange "nondewetting" membrane over a simpler prewet PTFE filter is that once the pores are wet, they will remain wet.[5] The issue encountered with hydrophobic PTFE-based filters is that dewetting causes the filter's pores to fill with gas, decreasing the available filtration area for flow. This would then increase the resistance across the filter element causing a loss in flow rate in the chemical bath.

Figure 3 provides an example of how a hydrophobic 0.05 µm PTFE-based filter can lose flow rate after multiple SC2 chemical bath exchanges. During each of these bath exchanges, the filter is exposed to ambient conditions which dewet the pores of the membrane filter. The non-dewetting QuickChange membrane maintains its flow rate and resistance at a constant value.

Outgassing cleaning and stripping chemistries are still being applied today in the semiconductor market but now with very strict particle control.

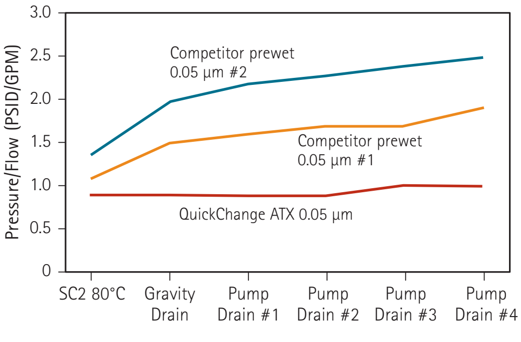


Figure 3. Dewetting test in SC2

Therefore, the use of <50 nm rated chemical filters is a requirement for the industry. As was previously stated, the tighter pore size rated filters will have increased dewetting nature if no process is implemented to increase its surface energy.

Gas-Locking:

Filters which are hydrophilic and/or nondewetting by their very nature will not allow undissolved gases to pass through them. The pores will maintain their wet state even in the presence of outgassing chemicals. However, the gas bubbles generated during wafer processing are still present and do come into contact with the filter. This phenomenon begs the question, what will happen to a nondewetting filter when gas bubbles are present? The undissolved gas bubbles are retained on the upstream side of the filter. If the filter housing is not efficiently vented, the gas bubbles can accumulate on the upstream sections of the filter and form a "wall" through which the liquid chemical behind it cannot penetrate. This phenomenon is commonly referred to as "gas-locking." Figures 4 and 5 illustrate conditions of poor and efficient venting for nondewetting filters, respectively and their effects on filter flow rates.

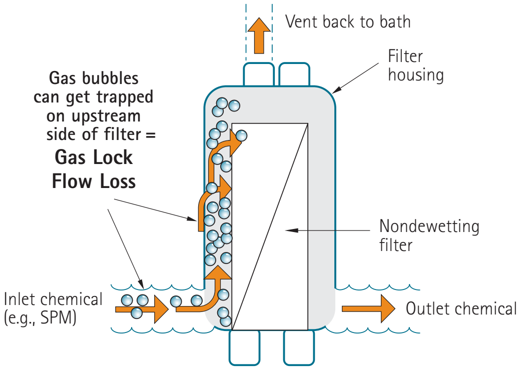


Figure 4. Gas-locking effect on nondewetting filter with poor venting

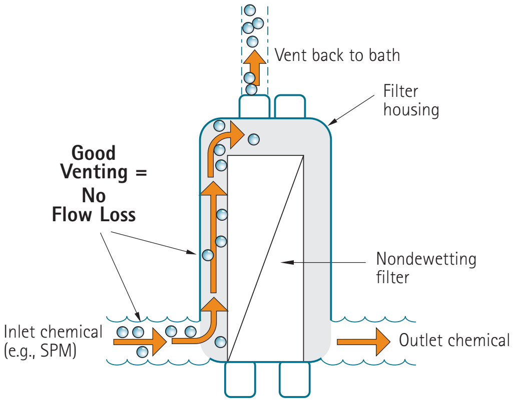


Figure 5. Efficient venting for nondewetting filter

[5] *This is the case as long as the water bubble point is not reached.*

So, in summary, dewettability and gas-locking phenomena can occur with the following conditions (Table 1).

TABLE 1. EFFECTS ON HYDROPHOBIC AND NONDEWETTING PTFE FILTERS ON BATH FLOW RATES

Filter	Possible Issues	Effect on Chemical Bath Flow Rate
Hydrophobic PTFE	Dewetting	Permanent flow loss (unless filter is cleaned, dried and rewet with IPA)
Nondewetting PTFE	Gas-locking if not efficiently vented	Temporary flow loss (until filter is vented)

Considerations for Venting Filter Modules

BOWL UP VS. BOWL DOWN

It is common practice for semiconductor equipment manufacturers and end-users to utilize a venting procedure for the filter housings in outgassing recirculating bath applications. The Entegris Chem-Line™ I style of the nondewetting filter family is commonly used in a T-Line style. The Chem-Line I T-Line style has the chemical inlet and outlet fittings located on the same horizontal axis. There are also several smaller fittings on module that can be used to vent or drain the filter depending on the orientation. Two of the vent/ drains are on the upstream side (before the fluid reaches the filter membrane) of the filter and two of the vent/drains are on the downstream side of the filter for the core-vent style filter.

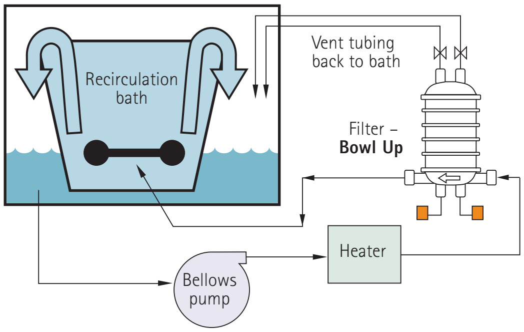


Figure 6a. Filter vented in bowl-up configuration

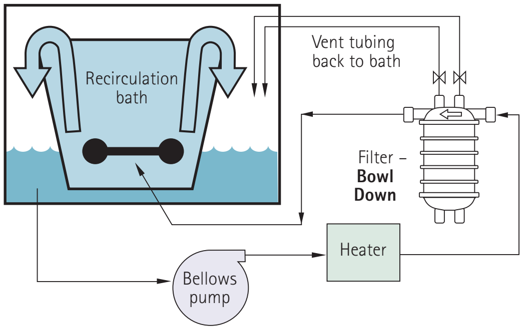


Figure 6b. Filter vented in bowl-down configuration

Typically this configuration of filters can be installed either in “bowl-up” or “bowl-down” configurations which are differentiated by the location of the vent fittings relative to the inlet and outlet. Figures 6a and 6b provide a schematic of the Chem-Line I T-Line style of the QuickChange filter for bowl-up and bowl-down configurations.

BOWL UP — STANDARD VENT VS. 90-DEGREE STYLE VENT

The Entegris Chem-Line style is available in both “standard” and “90-degree” style venting configurations. For bowl-down applications it is recommended that the 90-degree style upstream vent is used for outgassing applications. The reason for this is that the 90-degree style upstream vent has the vent rotated 90 degrees away from the main inlet fitting. This design feature allows the gas bubbles to work their way up to the vent more efficiently. With the standard style of upstream vent, the high liquid flow rate past the vent opening can sometimes prevent the gas bubbles from reaching the vent effectively. High liquid flow passed through the standard upstream vent can create a small venturi resulting in a negative pressure on the upstream vent causing poor venting efficiency. By rotating the vent by 90 degrees, the vent is out of the high flow regime and accessible to the gas bubbles rising from the bowl. Figures 7a and 7b provide a cross-section on the top cap of the Chem-Line I comparing the standard and 90-degree style vents.

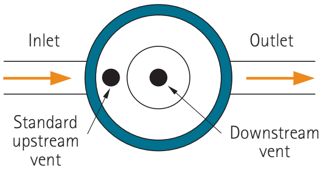


Figure 7a. Cross-section of top cap for Chem-Line I —“standard vent”

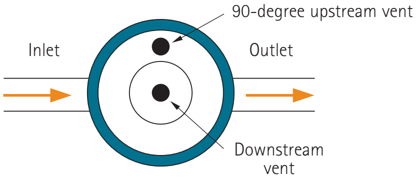


Figure 7b. Cross-section of top cap for Chem-Line I —“90-degree vent”

Venting Efficiency Experiments

Bowl Up vs. Bowl Down

The effects of pressure drop and gas locking were tested using a simulated application with DI water at room temperature and pressurized air representing the gas bubbles found in outgassing applications. The upstream and downstream fittings of the filter were connected to a pressure transducer to measure pressure drop and the flow rate was measured using a rotameter. The upstream vent also had a tee with a ¼″ PFA tube with a ⅛″ PFA tube inside of it and a valve at the end of the tube to restrict the venting. This simulates the orifice currently used to control venting in the customer's tool. A tee was placed before the filter which a ¼″ pressurized air line connected to it with a pressure regulating valve. This is used to sparge air into the system, simulating an outgassing bath. A valve was placed downstream of the filter to apply back pressure to the filter. Figure 8 provides a schematic of the setup.

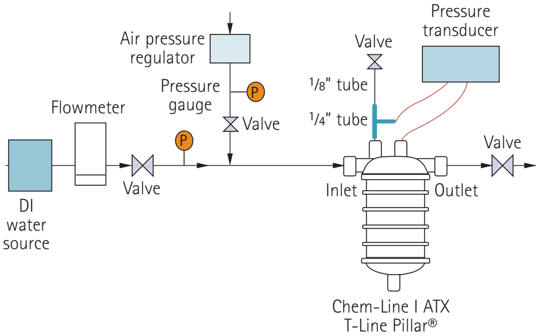


Figure 8. Experimental setup of simulated customer application

The initial pressure drop with no air sparge was measured and recorded.

The following test procedure was followed to simulate gas bubbles:

1. Flow water at 4 L/min.
2. Measure the initial pressure drop with no air sparge.
3. Open upstream valve connected to ⅛″ tube which is connected to upstream vent.
4. Open air valve and set pressure to 10 PSIG.
5. Hold for 10 seconds (during this time a lot of bubbles can visually be seen in the DI water and in the line connected upstream vent on the ⅛″ tube).
6. After 10 seconds, close the air valve and close the valve on the upstream vent connected to ⅛″ tube.
7. Measure pressure drop across the filter.

Under some conditions, the pressure drop of the filter increased. The following test procedure was followed to try to bring the pressure drop back down:

1. Close the downstream valve after the filter completely and hold for 10 seconds.
2. Open the upstream valve connected to the ⅛″ tube and the upstream valve on the pressure transducer.
3. Wait for about 30 seconds (during this time, excessive amounts of bubbles can be seen coming out of the vent lines).
4. Re-close all vent valves and allow for flow again.
5. Measure pressure drop.

Figure 9 shows a graph of the results for the standard vent in the bowl down orientation. Initially the pressure drop was normal but then rose significantly after air sparging and then decreased almost back to normal after applying back pressure.

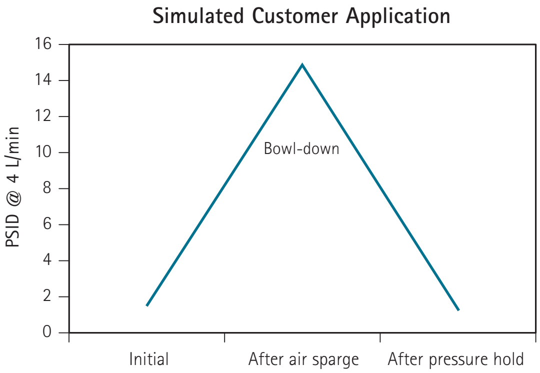


Figure 9. Nondewetting filter is gas-locking but not dewetting

Because the filter's pressure drop returned to normal for the QuickChange filter after back pressure and effective venting, the temporary increase in pressure drop is not dewetting. The higher pressure drop is due to inefficient venting. The gas cannot pass through the water coming into the housing to reach the small ⅛″ orifice efficiently enough.

To prove this theory, tests were rerun with a bowl-up configuration which should not have venting issues, since the inlet flow is now at the bottom. Figure 10 provides a summary of the results.

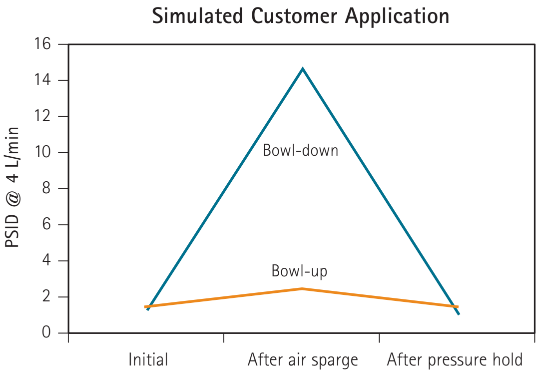


Figure 10. Bowl-up configuration does not gas-lock as severely as bowl-down

Bowl Down – Standard Vent vs. 90-Degree Style Vent

The air sparging experiments were conducted comparing a bowl-down standard vs. a bowl-down 90-degree style upstream vent. The results showed that the 90-degree style vent was much more efficient at bubble clearance, resulting in less of a pressure drop increase. Figure 11 provides a summary of the results.

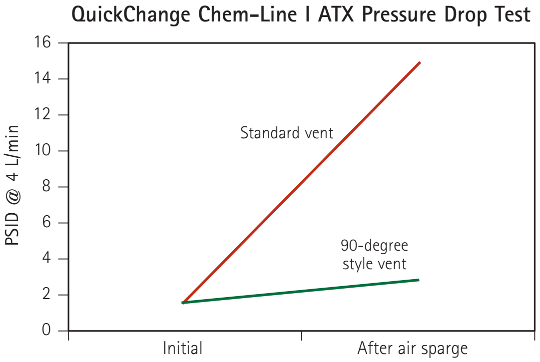


Figure 11. 90-degree style vent is more efficient in bubble clearance for bowl-down

High vs. Low-resistance Filter

The recently introduced QuickChange ATE and Torrento ATE product families have various design features which provide several advantages for filtering outgassing chemical applications. These features include the nondewetting PTFE membrane as well as low pressure drop across the filter elements. Low pressure drops are desirable as the filter can play a major role in determining the final application flow rate in recirculated bath systems.[6]

The pressure drop across a microporous filter is considered to be laminar flow. This means that pressure drop is proportional to both flow rate and viscosity. A filter's resistance can be determined by measuring its pressure drop at a particular flow rate and viscosity. Typically these resistances are expressed in terms of PSID/GPM-cP.

Figure 12 provides an example on the filter resistances of three Entegris nondewetting filters. Note that despite the 20 nm rating, the Torrento product has a lower resistance than any of the 30 nm options.

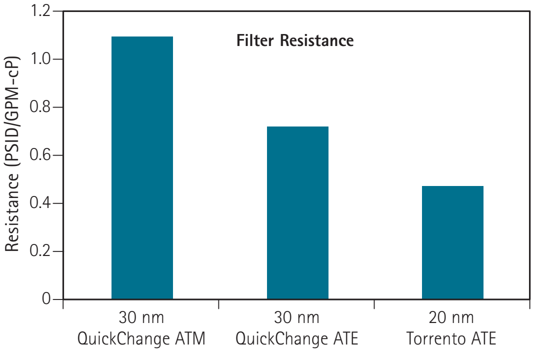


Figure 12. Filter resistance comparisons

Because both the QuickChange and Torrento products families are nondewetting, it is important to vent the housings efficiently to prevent gas-locking, which may cause a loss in flow rate. However, the venting efficiency is affected by the flow rate of the outgassing chemical through the upstream vent.

The flow rate through the upstream vent is largely determined by the resistance of the filter and the resistance of the flow path in the upstream vent. In other words, if the filter has a very low resistance, there may not be enough driving force to force the gas-liquid mixture up through the upstream vent lines back to the bath. This can be alleviated by lowering the resistance through the upstream vent lines by removing valves and/or increasing the inner diameter of the vent tubing.

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[6] *Frometa et.al, "Providing the Semiconductor Industry Filtration Solutions for 300 mm High Flow and Higher Viscosity Recirculated Applications", Entegris Application Note.*

Upstream Vent Flow Rate Experiment

A set of experiments were conducted in which the following filters were tested:

TABLE 2. FILTERS TESTED FOR FLOW RATE THROUGH VENT EXPERIMENT

Part Number	Filter	Configuration	Fittings	Upstream Vent
QCVYATE4S	30 nm QuickChange ATM	Chem-Line I	1-in S300 Pillar	90-degree style
QCVYATM4S	30 nm QuickChange ATE	Chem-Line I	1-in S300 Pillar	90-degree style
TRVXATE4S	20 nm Torrento ATE	Chem-Line I	1-in S300 Pillar	90-degree style

Each filter was set up in a bowl-down orientation. 20 L/min of DI water was passed through the filter and the pressure drop was measured across the upstream and downstream vent fittings.

A tee was placed on the upstream vent and a reducing fitting was connected to this tee. The other side of the reducing fitting was connected to 6 feet of PFA tubing of various inner diameters. The IDs (inner diameters) tested are listed in Table 3.

TABLE 3. FILTERS TESTED FOR FLOW RATE THROUGH VENT EXPERIMENT

Tubing	Vent ID
1/4" standard wall	3.96 mm
1/4" thin wall	4.83 mm
3/8" standard wall	6.38 mm
3/8" thin wall	8.00 mm
1/2" standard wall	9.55 mm

A schematic of the vent flow rate experiment is shown in Figure 13.

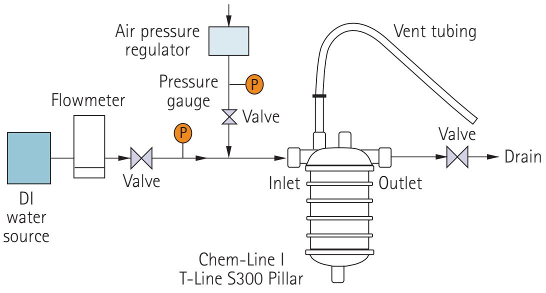

Figure 13. Schematic of vent flow rate experiment

The total flow rate to the filter was set at 20 L/min and the flow rate which bypassed the filter through the 6 feet of vent tubing was measured manually for each case. Figures 14a, 14b and 14c show the results in all three filter cases with the varying vent tubing diameters. As is expected, the amount of liquid flow rate through the upstream vent increases with increasing vent inner diameter.

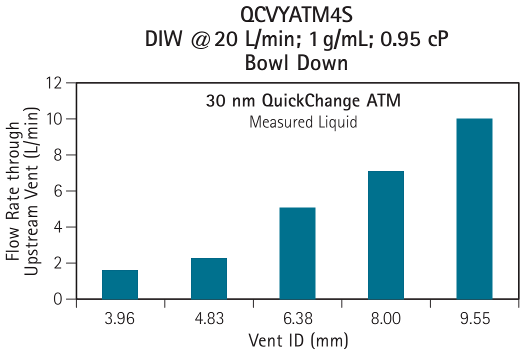

Figure 14a. 30 nm QuickChange ATM — flow rate through upstream vent vs. ID

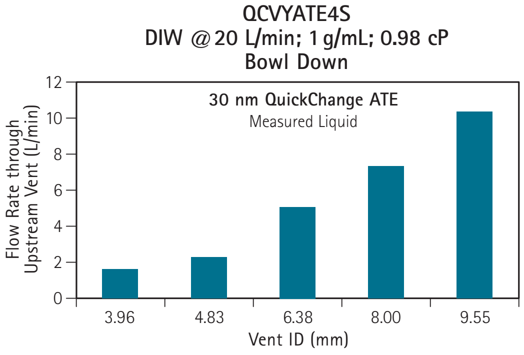

Figure 14b. 30 nm QuickChange ATE — flow rate through upstream vent vs. ID

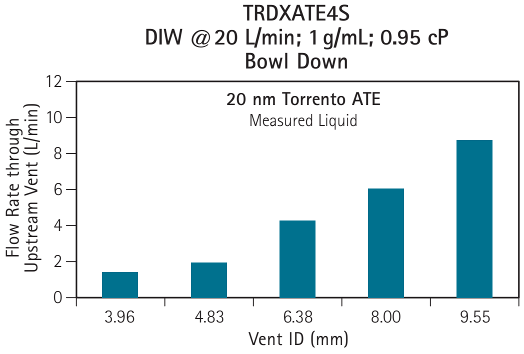

Figure 14c. 20 nm Torrento ATE — flow rate through upstream vent vs. ID

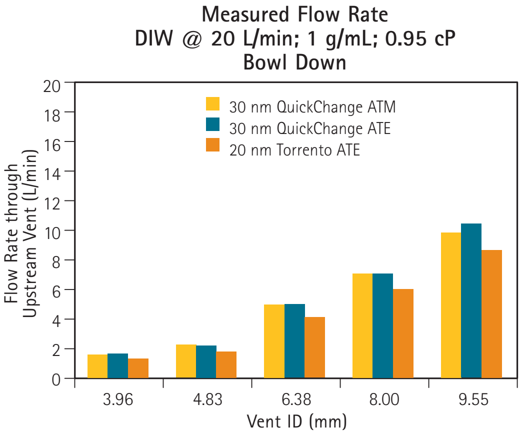

Figure 15. Upstream flow rate comparison

Plotting the three sets of filters together shows that the larger the vent tubing ID, the more flow will pass through the vent line. However, the lowest resistance filter, which is the 20 nm Torrento, had the lowest flow rate relative to the 30 nm filter options. Figure 15 provides a summary of the upstream flow rate results.

Summary and Recommendations

1. It is important to vent the housing for outgassing applications. This eliminates a pressure drop due to gas-locking that can lead to flow restriction.
2. The flow rate in the bath will be dependent on the filter, fitting size and venting efficiency as well as pump size.
3. If the chemistry is outgassing such as SPM/SC1, then very efficient venting is required.
4. To achieve maximum venting efficiency, do the following:
   - Consult with Entegris and OEM tool maker.
   - Bowl-up configuration does not gas-lock as severely as bowl-down standard venting.

     For bowl-down configuration:
     - 90-degree style venting is much more efficient at bubble clearance.

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