# Use of Nickel and 316L Stainless Steel Filter Assemblies in High Purity Corrosive Gas Distribution Systems

**Use of Nickel and 316L Stainless Steel Filter Assemblies in High Purity Corrosive Gas Distribution Systems**

*J. O' Sullivan, Ph.D.*

## Introduction

In addition to meeting the requirements of ultra high purity bulk gas distribution systems, the distribution of specialty and corrosive gases necessitates that the gas distribution system is corrosion resistant and does not exhibit any catalytic behavior. Vereecke[1] and coworkers reported that reaction between reactive gases and materials of construction employed in gas delivery systems can result in the formation of corrosion by-products, which may contaminate the gas stream as both particles and volatile metal complexes, depending on their relative vapor pressure.

To ensure the highest quality gas at the point-of-use (POU), efforts have focused on the selection of the appropriate materials for construction of the distribution system. Traditionally, 316L stainless steel has been employed in the construction of subcomponents for use in reactive gas distribution systems. The proper selection of the stainless melt can improve the corrosion resistance in UHP gas systems. In the case of high purity semiconductor gas filter assemblies, it is important to specify the proper chemistries, grain size and inclusions[2]. In addition, the suitability of the material to be formed, mechanically polished, and electropolished (EP) must also be evaluated. The careful selection of the 316L stainless steel utilized in the fabrication of filter assemblies is critical, as materials of similar composition can perform very differently.

Wang and coworkers noted variability in the corrosion behavior of steel alloys with bulk compositions that are virtually identical when exposed to moist HCl[3]. Smudde et al.[4] observed that when moisture is below 1 ppmv, bromine from HBr is not incorporated beyond the native oxide of 316L stainless steel and no macroscopic degradation of the metal occurs. Fine and coworkers[5] confirmed the latter observations by investigating the effect of moisture content on the extent of HBr corrosion for 316L electropolished stainless steel. The scanning electron microscopy (SEM) and x-ray emmision spectroscopy (XES) analysis of the exposed sample coupons indicated no effect upon exposure to HBr containing less than 0.5 ppm of moisture. A moisture content of 10 ppm resulted in bromide incorporation and the onset of corrosion. The formation of corrosion pits was noted upon increasing the moisture level in the HBr to 100 ppm. A dense bromide scale was noted at a moisture concentration of 1,000 ppm.

Corrosion is typically quantified by techniques such as trace gas analysis, change of surface morphology, particle shedding and leakage. Wang and coworkers[6] estimated the lifetime of EP 316L stainless steel tubing in HCl service, containing 1 ppm of moisture, to be of the order of 2-3 years based on particle shedding due to corrosion. The latter value is in agreement with field experience. The extrapolated lifetime of EP 316L stainless steel tubing at various moisture concentrations is shown in Table I. The extrapolated lifetime is based on the time required to produce 10 particles/scf at a flow rate of 3.531 scfm (100 slpm).

**Table I**
Extrapolated Lifetime of 0.25 - in. Tubing [10 particles/scf at 3.531 scfm (100 slm)]

| $H_2O$ (ppm) | Lifetime |
|---|---|
| 5 | 170 Days |
| 2 | 425 Days |
| 1 | 2.3 Years |

| 0.5 | 4.7 Years |
|-----|-----------|
| 0.2 | 11.6 Years |
| 0.1 | 23.3 Years |

A number of maintenance practices are recommended to eliminate the introduction of moisture into the corrosive gas distribution system[7]. It has been demonstrated that if adequate purge and evacuation procedures are followed to remove corrosive gases (such as HBr), EP 316L stainless steel can be exposed to moist air without diminishing the initial surface quality. However, if the purge and evacuation procedures are not followed, iron and bromine rich crystalline deposits form on the surface.

In order to maintain higher purity in corrosive gas service, new materials of construction have been investigated as a possible replacement for 316L stainless steel. One of the materials being investigated is nickel as it is corrosion resistant in aggressive environments. Nickel, however, is also a reactive material, commonly used as a hydrogenation catalyst.

The thermal decomposition characteristics of active specialty gases on various metal surfaces were investigated by Prof. Ohmi and his group at Tohuku University[8]. The metal surfaces investigated included nickel, oxygen passivated 316L stainless steel, chromium passivated 316L stainless steel, and 316L stainless steel with an electropolished (EP) surface. The thermal decomposition of the active specialty gases was monitored with the aid of a gas chromatograph (GC) and a Fourier Transform Infrared Spectrometer (FTIR). The FTIR was utilized to monitor the specialty gas concentration exiting the test sample (0.25" diameter, 1 m long tube). In the case of phosphine, 100 ppm of phosphine in argon was passed through the tube at a flow rate of 5 sccm. The nickel sample exhibited a strong catalytic effect on the phosphine decomposition (see Figure 1). The nickel surface reduced the phosphine concentration to undetectable levels at a temperature of 55°C. In contrast, the EP 316L stainless steel sample resulted in complete thermal decomposition of the phosphine gas at 260°C. The chromium passivated 316L stainless steel surface resulted in complete thermal decomposition at 370°C.

**Figure 1**
Thermal decomposition of phosphine (100 ppm) on various surfaces
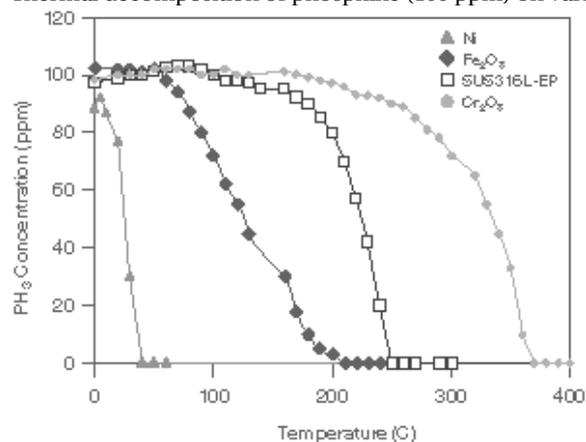


In addition to the metal surfaces listed above, Ohmi investigated the catalytic effect of a nickel filter on thermal decomposition of silane. The 1,000 ppm silane gas in argon was passed through the nickel filter at a flow rate of 5 sccm. Initially the gas was introduced at room temperature. No silane was detected at the outlet of the filter for 150 minutes (see Figure 2). After 150 minutes silane was detected, and the silane level increased to a level of approximately 800 ppm. The fact that

**Figure 2**
Thermal decomposition of silane (1,000 ppm) on a nickel filter at a flow rate of 5 cc
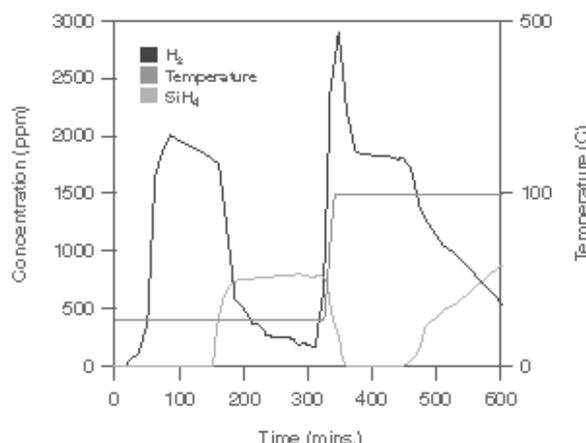
1,000 ppm of silane was not detected after 330 minutes suggests that the catalytic decomposition of silane continued to occur. Upon increasing the temperature to 100°C, a large spike was observed in the hydrogen concentration due to further decomposition of silane. Further testing of silane with nickel filters at flow rates typical of actual use conditions suggests that the nickel surface is readily saturated and that minimal thermal decomposition of the gas occurs9 after the surface saturation occurs.

The results outlined above for nickel surfaces suggest that due consideration must be given to the corrosion resistance and the catalytic behavior of a material when selecting materials for use in reactive gas service. In the case of a POU gas filter assembly, the selection is critical as volatile corrosion by-products will enter the process tool.

**316L Stainless Steel Media and Nickel Media in Corrosive Gas Service**

The purpose of the SEMI document "Test Method for Evaluation of Particle Contribution from Gas System Components Exposed to Corrosive Gas Service" (Draft Doc. # 2572) is to provide a test method to compare gas handling components for potential particle generation in corrosive gas service. The document is intended as a practical means of generating performance data for a group of components to be compared in a selection process.

A flow chart of the sequence of exposure of gas handling components to corrosive service and the subsequent determination of the particle contribution is shown in Figure 3. The test sequence was used to compare the corrosion resistance of a gas filter assembly employing nickel media and a gas filter assembly employing 316L stainless steel media.

**Figure 3**
Summary of test method sequence employed in SEMI Draft Document # 2572
"Test Method for Evaluation of Particle Contribution from Gas System Components
Exposed to Corrosive Gas Service".
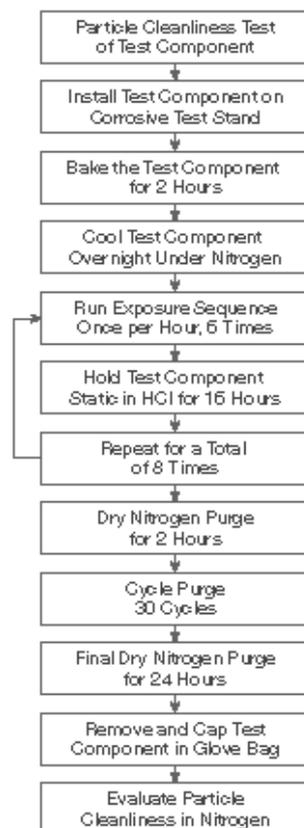


The Ultramet-L™ Gaskleen®1100 filter assemblies are constructed of an EP 316L stainless steel housing and a media pack (nickel or 316L stainless steel) of sintered metal fiber of a specified diameter. The housing of the assemblies has an internal surface finish of < 7 μ in $R_a$ and a chromium enriched surface layer[10].

The gas filter assemblies in question were initially subjected to a particle cleanliness test. The particle cleanliness test was based on the SEMATECH SEMASPEC #93021511A-STD, "Test Method for Determination of Particle Contribution by Filters in Gas Distribution Systems". This test consists of a 45 minute steady flow test, followed by a 45 minute dynamic test, and finally a 10 minute impact test. The nitrogen test flow rate was 10 lpm at an inlet pressure of 30 psi. The particle cleanliness testing was conducted in a class 1,000 cleanroom. The particle levels downstream of the test filter assemblies were monitored with a Condensation Nucleus Counter (CNC, Model 3025, from TSI Inc, Minneapolis, MN), sampling at a flow rate of 0.01 scfm for particles larger than 0.003 μm in size.

After completion of the particle cleanliness test, the test component was removed from the aerosol test stand and capped in a glove bag under nitrogen purge. The capped test component was then transferred to the HCl exposure test stand. A schematic of the exposure test stand is shown in Figure 4. All components and tubing employed in the test stand were constructed of EP 316L stainless steel surfaces. Where possible VCR fittings were used. The test filter assembly was installed on the exposure test stand employing a glove bag, while maintaining a positive nitrogen purge. The exposure test stand (between V5 and V1) was baked for two hours at 70°C while maintaining the purified nitrogen purge (< 1 ppb moisture) at a test flow rate of 500 cc/min.

**Figure 4**
Test Stand Employed for Corrosive Gas Exposure
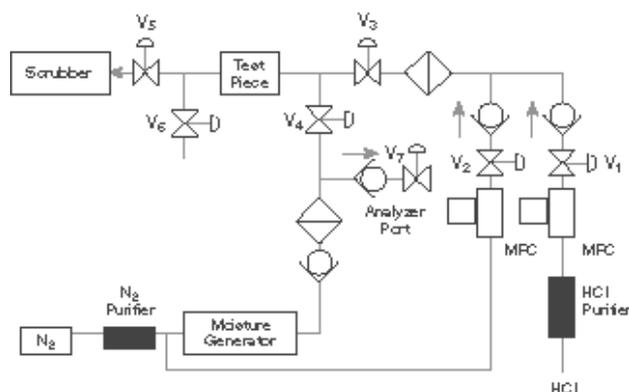


After overnight cooling under nitrogen purge, the HCl exposure was commenced. The HCl exposure sequence is shown in Table II. The HCl exposure was run once per hour for six hours. After completion of the sixth exposure, the test filter assembly was held in static HCl for 18 hours (SEMI method specifies 16 hours). The exposure cycle described above was repeated a total of eight times. The exposure cycle was suspended over the weekend and a dry nitrogen purge was maintained. The HCl exposure was resumed at the start of the next work week. The moisture content was monitored with the aid of a Meeco Aquamatic + moisture analyzer (Meeco Inc., Warrington, PA) to ensure that a constant moisture content of 100 ppm in the nitrogen stream was maintained. The HCl was purified to < 100 ppb of moisture by the use of a Pall Gaskleen™ Purifier (GLPV2HCLVMM4), which is resin based.

**Table II**
Exposure sequence for test component

| Step | Time (minutes) | Condition |
|---|---|---|
| 1 | 5 | Flow dry N2, 0.5 slpm |
| 2 | 10 | Flow wet N2 – 100 ppm H2O, 0.5 slpm |
| 3 | 5 | Flow dry HCl, 0.5 slpm |
| 4 | 40 | Stagnant HCl, no flow |

The probability of particle generation by a test component when subjected to the corrosive exposure sequence described above is supported by previous reports of particle generation by EP 316L stainless steel tubing after exposure to moist HCl (100 ppm) for 8.5 days. As previously reported, Wang et al.[6] estimated the lifetime of EP 316L stainless steel tubing based on the time required to generate 10 particle/scf at a flow rate of 3.531 scfm (100 slpm). In addition, Fine and coworkers[5] noted that 200 ppm of moisture is required for condensation of liquid HBr, while the onset of corrosion is noted at 100 ppm.

The test filter assemblies were subjected to a 2 hour dry nitrogen purge following completion of the eight day HCl exposure. The test stand was subjected to a cycle purge for 30 cycles in order to remove any traces of HCl from the test component. The cycle purge consisted of 20 seconds of rough vacuum followed by 10 seconds of pressurization with dry nitrogen to 80 psig. The test filter assemblies were subjected to a final 24 hour purge with dry nitrogen prior to removing the test component from the exposure stand. The final purge with dry nitrogen was performed at a low flow rate to ensure that no particles generated by the exposure were removed.

The capped test component was then transferred back to the cleanroom for particle cleanliness testing in purified nitrogen. After completion of the particle cleanliness testing, the exposed filter assemblies were sectioned and subjected to microscopic analysis to determine the extent of corrosion of the 316L housing, 316L stainless steel media pack and the nickel media pack. The effects of corrosion were analyzed in terms of surface roughening, change in fiber diameter, pitting and localized corrosion at the weld interface between the assembly housing and the media pack.

## Test Results and Discussion

**Particulate Cleanliness Testing:** The particle levels detected downstream of the test filter assemblies during the particle contribution testing prior to HCl exposure and immediately after HCl exposure are shown in Table III. The particulate levels detected downstream of the Ultramet-L™ Gaskleen® 1100 Series Assembly (GLFF1100VMM4) and the Ultramet-L™ Gaskleen® Nickel Media 1100 Series Assembly (GLFN1100VMM4) immediately after the HCl exposure were within background levels. The latter result indicates that no particulate corrosion by-products were generated during the HCl exposure in the case of the nickel media and the 316L stainless steel media.

**Table III**

| Filter | Steady Flow Test (cts/ft3) | Dynamic Flow Test (cts/ft3) | Impact Test (cts/ft3) |
|---|---|---|---|
| GLFF1100VMM4 Pre-Exposure | 1 | 1 | 1 |
| GLFF1100VMM4 Post-Exposure | 1 | 1 | 1 |
| GLFN1100VMM4 Pre-Exposure | 1 | 1 | 1 |
| GLFN1100VMM4 Post-Exposure | 1 | 1 | 1 |

The absence of any particle corrosion by-products for the nickel media is not unexpected as nickel is a corrosion resistant material. The results obtained for the 316L stainless steel media suggests that the material is corrosion resistant under the conditions typically experienced in a semiconductor UHP specialty gas distribution system. Previous reports have indicated that Ultramet-L™ Gaskleen® 4400 (316L stainless steel media) filter assemblies remain suitable for use in semiconductor gases after more than two years service in $BCl_3$, HBr and $Cl_2$[11].

**Microscopic Inspection:** In addition to monitoring the extent of corrosion in terms of particle shedding, the exposed samples were sectioned and subjected to microscopic inspection to determine any changes in surface morphology.

The internal housing surface finish of the upstream and downstream sections of the HCl exposed filter assemblies, including inlet and outlet bore, were measured to be < 7 μ in $R_a$. The measured surface finish of the filter assemblies exposed to moist HCl is within the maximum internal surface finish specification of the 1100 Series Ultramet-L™ Gaskleen® filter assembly. The fine surface finish exhibited by the exposed assemblies suggests that the internal surfaces of the filter assemblies were not subjected to corrosion. The fine surface finish is not unexpected as the Ultramet-L filter assemblies possess a chromium enriched surface layer which enhances the corrosion resistance of EP 316L stainless steel surfaces.

Previous reports have indicated that EP stainless steel is susceptible to aggressive corrosion caused by halogen containing gases, specifically in weld areas[12]. The most significant types of corrosion are intergranular corrosion, general surface corrosion and pitting corrosion. In the case of weld areas, the corrosion typically occurs in the heat affected zone (HAZ) or downstream of the weld with respect to the purge gas flow. The extent of corrosion is strongly influenced by the number of inclusions, presence of volatile impurities (manganese and copper), and the levels of carbon and sulfur[13].

The weld regions of the Ultramet-L Gaskleen 1100 Series Assembly (GLFF1100VMM4) and the Ultramet-L Gaskleen 1100 Series Assembly with Nickel Media (GLFN1100VMM4) revealed no evidence of corrosion (see Figures 5 and 6). The absence of any particle corrosion by-products, as evidenced in the particle cleanliness testing, is in agreement with the corrosion-free weld regions observed. The corrosion-free weld regions observed for the exposed filter assemblies illustrates that the proper selection of raw materials (chemistry and processing technique) combined with refined manufacturing techniques strongly influence the corrosion resistance of a stainless steel component[2].

**Figure 5**
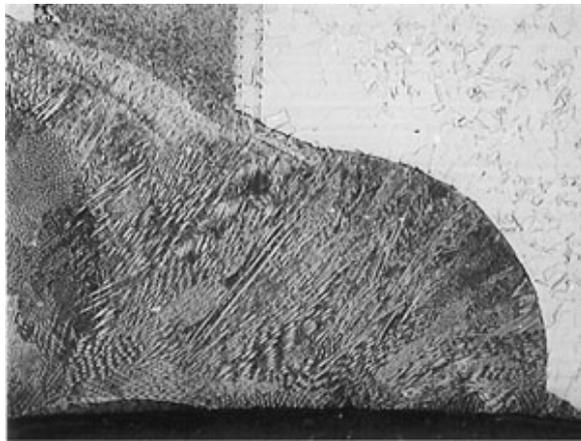Weld Region Stainless Steel Filter (GLFF1100VMM4)

**Figure 6**
Weld Region Nickel Filter (GLFN1100VMM4)



The internal surface area of the assembly housing is less than 1% of the total BET surface area of the filter assembly. The higher surface area of the medium pack suggests that corrosion is most likely to occur at the medium pack. The upstream and downstream sintered woven 316L stainless steel mesh support layers of the Ultramet-L™ Gaskleen® filter assembly and the nickel mesh support layers of the Ultramet-L Gaskleen filter assembly with nickel media subjected to the HCl exposure revealed no corrosion.
The diameter of the sintered 316L stainless steel fibers of the media pack from the filter assembly exposed to HCl was determined with the aid of a scanning electron microscope (SEM) and compared to a filter assembly supplied from manufacturing stock. The diameter of the 316L stainless steel fibers from the returned filter assemblies is identical to that of the filter assembly removed from manufacturing stock (see Figures 7 and 9). The SEM photomicrographs revealed some contamination (scaling) but no degradation of the sintered fibers. The particulate cleanliness observed for the Ultramet-L Gaskleen 1100 Series after the HCl exposure is further evidence that no degradation of the 316L stainless steel media pack occurred during exposure to the moist HCl.

**Figure 7**
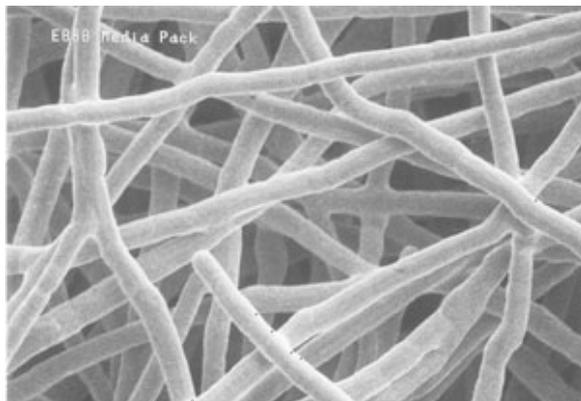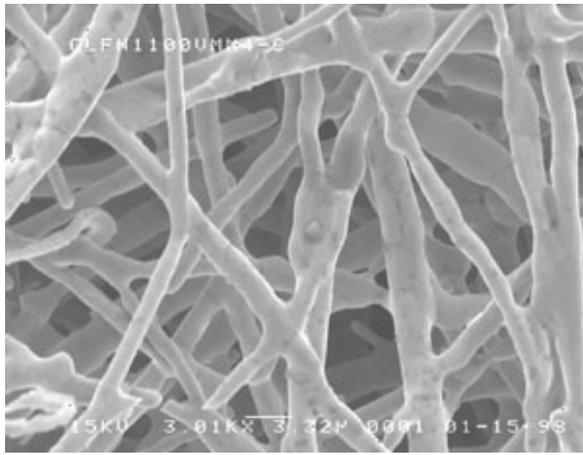316L Stainless Steel Fibers - Control



**Figure 8**
Nickel Fibers - Control

Similarly, the diameter of the sintered nickel fibers of the media pack from the filter assembly exposed to HCl gas was determined with the aid of a SEM and compared to a filter assembly supplied from manufacturing stock. The diameter of the nickel fibers from the returned filter assemblies is identical to that of the filter assembly removed from manufacturing stock - see Figures 8 and 10. The SEM photomicrographs revealed no degradation of the sintered nickel fibers. The particulate cleanliness observed for the Ultramet-L™ Gaskleen® 1100 Series with the nickel media after the HCl exposure is further evidence that no degradation of the nickel media pack occurred during exposure to the moist HCl.

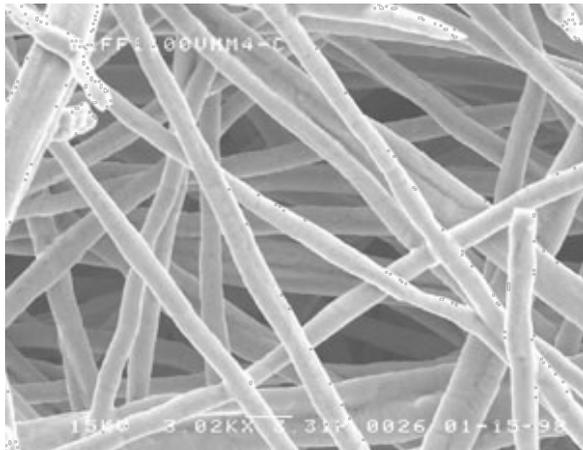**Figure 9**
316L Stainless Steel Fibers - Test Component



**Figure 10**
Nickel Fibers - Test Component

## Conclusions

The Ultramet-L Gaskleen 1100 Series assemblies with 316L stainless steel media and nickel media evaluated in moist HCl gas revealed no evidence of the generation of particles due to corrosion. The particulate cleanliness of the assemblies after exposure to moist HCl gas was observed to be within background levels, even under dynamic and impact test conditions. In addition, the assemblies displayed a high surface finish and no evidence of corrosion or degradation of the media packs. The latter observations indicate that the 316L stainless steel media pack and the nickel media pack are corrosion resistant under the normal service conditions experienced in a semiconductor corrosive gas distribution system. In the case of active specialty gases, such as arsine, phosphine and silane, however, consideration must be given to the catalytic behavior of various metal surfaces. Through our experience, with this study and a previous study where no degradation was noticed at a period of more than 2 years for returned filter assemblies employed in corrosive gas service[11], we suggest that in a effort to maintain good housekeeping practices that gas filters should be changed out every two years.

Top

## References

1. "Generation and Transport of Corrosion Products in HCl Gas Lines", G. Vereecke, M.M. Heyns, N. Anderson, C. Elsmore and P. Espitalier-Noel, *Future Fab International,* p. 283, Issue 2, Volume 1, 1997.

2. "Selection of 316L Stainless Steel For High Purity Semiconductor Gas Filter Assemblies", W. Murphy and B. Gotlinsky, Solid State Technology, Contamination Control Supplement, May 1995.

3. "Using Atomic Force Microscopy to Evaluate Alloys for Corrosive Gas Service", H.W. Wang and S. Chesters, *Microcontamination,* June 1994.

4. "Materials Selection for HBr Service", G.H. Smudde, W.I. Bailey, B.S. Felker, M.A. George and J.G. Langan, *Corrosion Science,* Vol. 37, p. 1931, 1995.

5. "The Role of Moisture in the Corrosion of HBr Gas Distribution Systems", S.M. Fine, R.M. Rynders and J.R. Stets, *J. Electrochemical Society,* Vol. 142, No. 4, April 1995.

6. "Estimating the Lifetime of Electropolished Stainless Steel (EPSS) Tubing in Corrosive Gas Service", H.W. Wang, G. Doddi and S. Chesters, *Journal of the IES,* p. 28, July 1994.

7. "The Effects of Corrosive Gases on Metal Surfaces", P.M. Clarke. R.A. Hogle and S.M. Lord, in Microcontamination '93 Conference Proceedings, p. 433, Canon Communications, Santa Monica, CA, 1993.

8. "The Evaluation of Thermal Decomposition Characteristics of Active Specialty Gases on Various Metal Surfaces Using FT-IR Method", T. Ohmi, Y Shirai, S. Lee and S. Miyoshi, Proceedings of the Institute of Environmental Sciences, p. 17, 1995.

9. "Compatibility of Silane with Nickel Filter Media", R. Binder, Productronica Exhibition, 1995.

10. "Filter Products for the Semiconductor Industry", p. 106-109, Second Edition, Pall Corporation, 1996.

11. "Recommended Change-out Schedule For Electronic Grade Filters- Case Study", J. O' Sullivan and B. Gotlinsky, STR-PUF 32.

12. "Investigating the Corrosion Resistance of Heat-Affected Zones in CrP Tubing", S. Krishnan, S. Grube, O. Laparra and A. Laser, p. 37, *Microcontamination,* May 1996.

13. "Effect of Stainless Steel Melt Methods on the Corrosion Resistance of Welds in UHP Gas Lines", C. Burton, Workshop on Gas Distribution Systems, SEMI 1997.

Top