Chemical and Supplier Management: Do's and Don'ts – How the Heck Did THAT Happen?

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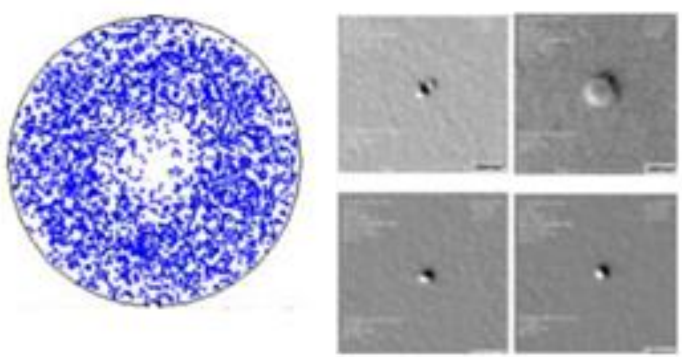
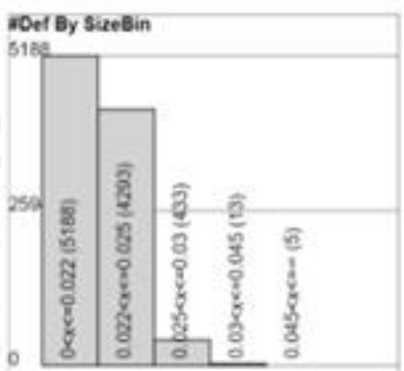
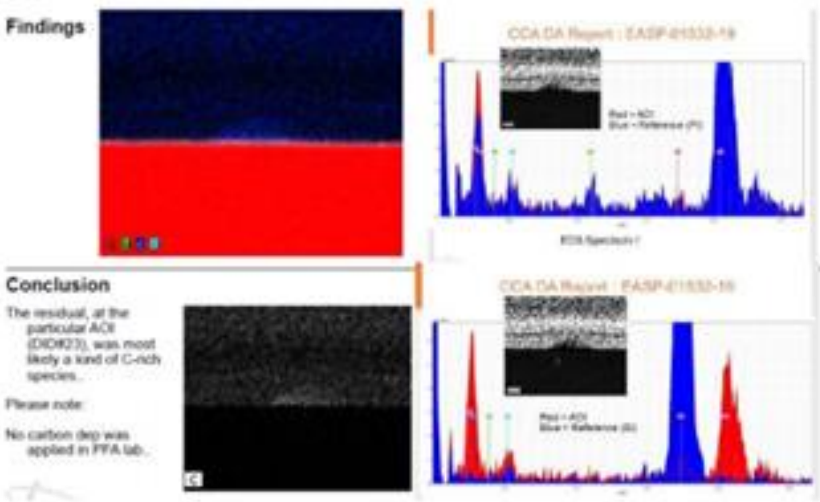
How the Heck did THAT Happen?

Problem Statement: Particle Count failures, defect looks embedded/residue type and EDX shows C-rich based on TEM analysis.







Agenda:

- Who are We?
- “Help Them Help Us”
- High Purity Chemical Specifications
- Why particle control?
- Where do particles come from?
- Particle Size Measurement
- Mechanisms of Filtration
- Recommendations for Particle Control
- How much does it cost?
- What else besides filtration?
- Does polishing help?
- Summary

A User’s Perspective…….

- Many of the presentations are from a suppliers perspective
  - Instrumentation for measuring chemicals, monitoring chemicals, chemicals themselves
- This presentation is from a user’s/customer’s perspective
- Who is GLOBALFOUNDRIES?

GLOBALFOUNDRIES locations……

Supplier Management

- “Help Them Help Us” Model
  - Revenue of many of our suppliers tied to only small % high purity
  - Historic processes vs. new requirements
  - Environmental disconnects: What’s a cleanroom?
  - Specifications that can’t be met with current processes
  - Traditional Quality Audits typically only point out flaws
  - Engineering teams working together to help solve technical issues

High Purity Chemical Specifications

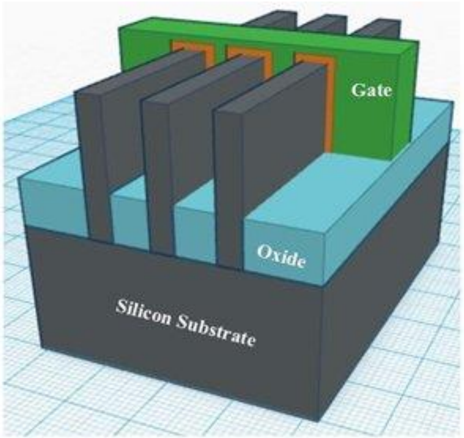
- Hundreds of chemicals used in a leading edge FAB today.
  - Highest Usage Bulk Chemicals include H_2O_2, NH_4OH, H_2SO_4, HCL, HF, HNO_3……

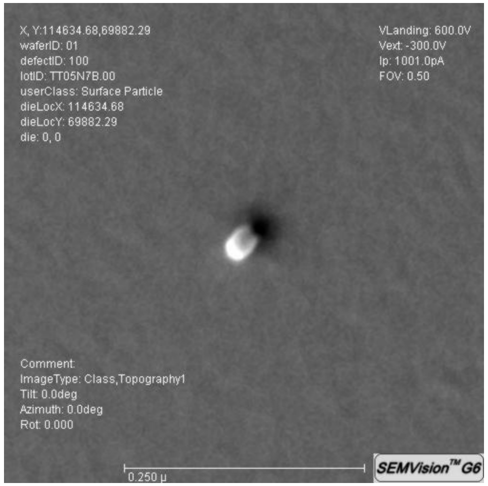
- Before 6-7 years ago, metallics were the major source of concern
  - Gate oxide leakage and integrity, shifts in voltage thresholds of transistor, pad corrosion, defectivity in the photoresist, others
  - Industry has done a pretty good job in cleaning them up
  - Now measured in parts per trillion – typically using ICP-MS

- Now at 7, 10, 14, 22 nm, number of particles and their sizes are more significant!
  - Gate oxide integrity, high resistivity contacts, pattern opens and shorts producing killer defects on the wafer

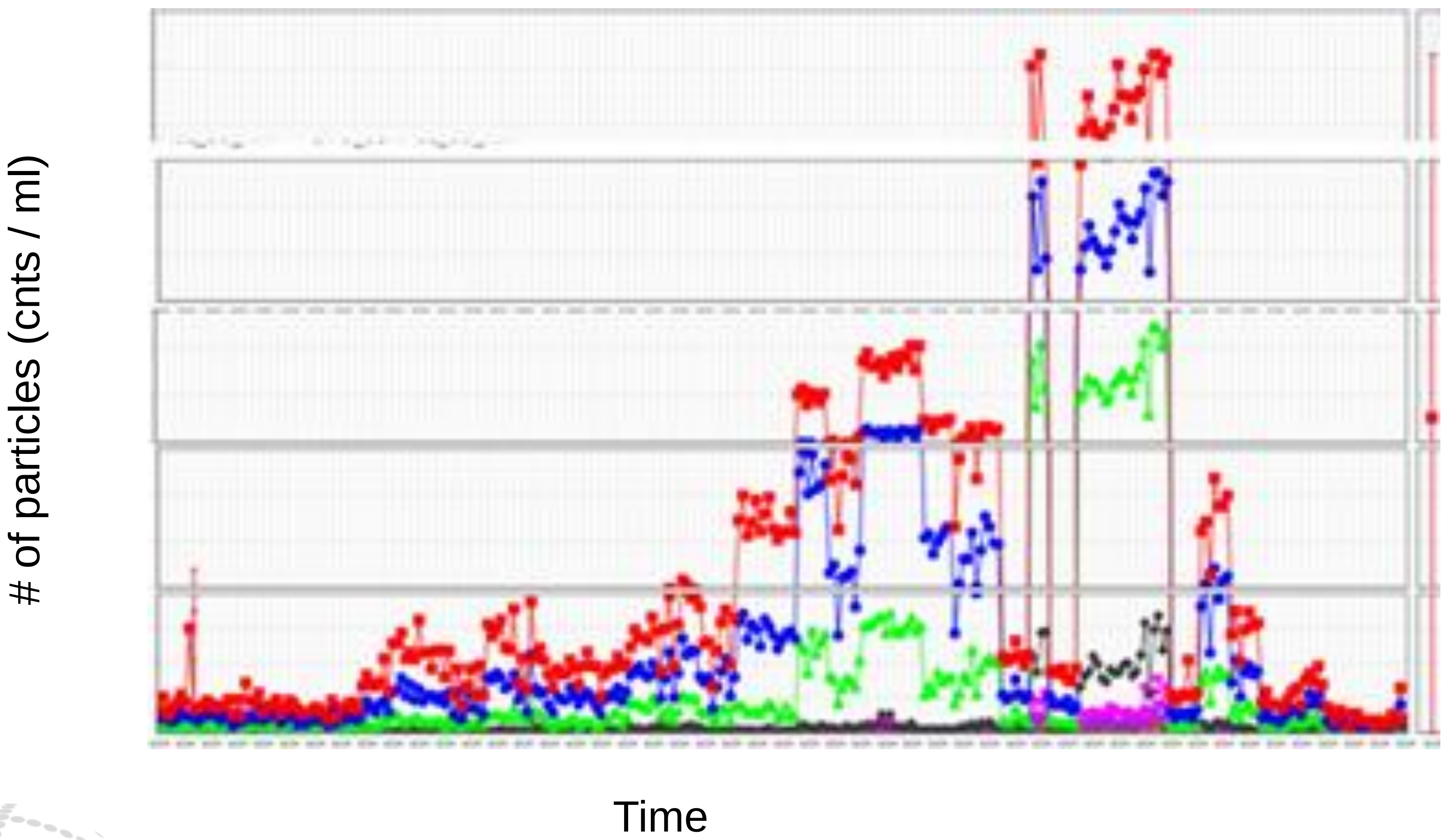
Why Particle Control?

- As semiconductor nodes become smaller and smaller, particle control becomes increasingly more important.
- For 14 nm node, it has been shown that a particle excursion in sulfuric acid, going from 50 counts / ml to 4000 counts / ml for sub-30nm particles, decreased yield by 30 percentages points!
- Same type excursions potentially have serious reliability implications as well.
- Will affect FINFET and Planar technologies at all nodes, depending on particle size vs. feature size (opens, shorts, high resistance….)



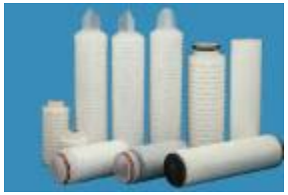


Particle Excursion Data at CLNS tools



Where do particles come from?

- **Supplier Process**
  - **Tanks**
  - **Valves**
  - **Lines**
  - **Pumps**
  - **Filters**
  - **Heat Exchangers**
- **Transportation**
- **Offload**
- **FAB Distribution System**
  - **Tanks**
  - **Valves**
  - **Lines**
  - **Pumps**
  - **Filters**
- **Tools**
  - **Tanks**
  - **Valves**
  - **Lines**
  - **Pumps**
  - **Filters**
  - **Environment**



Transportation of High Purity Chemicals

- Isotainers: Planes, trains, and automobiles!
  - High purity PFA lined Stainless Steel Containers on wheels
  - Often “owned” by supplier and dedicated to a particular customer
  - Leaching, qualification, usage
    - Leached in water, measured for metals, particulates
    - Leached in chemical of choice measured for metals, particulates
- Cost often largely based on transportation distance!
- Delivery often limited by……drivers!

Transportation Containers

- Isotainer, Isotanker, Tankwagon….
  - Typically stainless steel lined with PFA or PTFE
  - Typically 15,000 - 25,000 Liters
  - Need to be commissioned/qualified across multiple weeks/months
    - Rinsed and leached with water and chemical, monitored for metallics and particles
  - Need to be internally inspected every few years
  - 80/20 rule for transportation

- Totes
  - Typically made of polymer, HDPE, other
  - Typically 275 gal = 1050 Liters
  - Need to be commissioned/qualified
- Barrels
  - Typically made of polymer, HDPE, other
  - Typically 55 gallons = 200 liters
  - Can have bladder

When choosing a shipping or storage vessel…

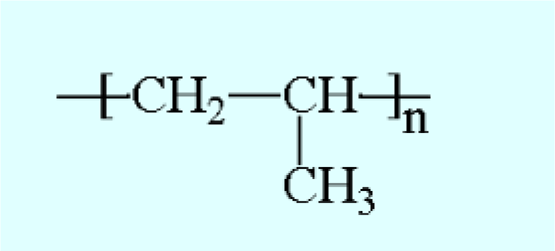
- Material of Choice: Must be able to stand up to chemical inside for specified time.
  - Polypropylene: One of the “dirtiest” and cheapest material available
  - PTFE/PFA: One of cleanest and most expensive materials available
  - Does transportation over long distances increase particle contamination?
  - Can it stand up to the chemicals it holds at the service/storage temperatures?
    - Start with Chemical Compatibility/Resistance Charts
    - Do leaching studies for time zero fail predictions

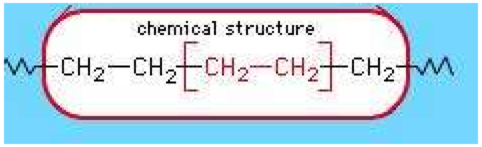
■ = Resistant   ● = Limited Resistance   ▲ = Not Resistant   * Resistance also dependent upon concetration, time, and temperature

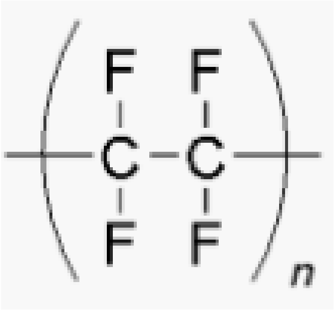
AGENTS, CONCENTRATION: WEIGHT-% / MATERIAL	ABS	Acetal (copolymer)	Acetal (homopolymer)	Noryl®	Nylon 6	PBT	PEEK	PET	Polycarbonate	Polyethylene	Polypropylene (homopolymer)	PPS	PPSU (Radel® R)	PSU (polysulfone)	PTFE	PVDF	Ultem®	Vespel® SP-1
Acetamide 50%	■		■		■										■	■		
Acetic acid, aqueous solution 5%	■	■	●	■	■	■	■	■	■	■	■	■	■	■	■	■		
Acetic acid, aqueous solution 10%	■	■	●	■	▲	●	■	●	■	■	■	■	■	■	■	■	■	●
Acetic acid, concentrated	▲	●	▲	■	▲	▲	▲	▲	▲	■	■	■		■	■			
Acetone	▲	■	■	▲	●	▲	■	▲	▲	●	■	■	▲	▲	■	●		■
Ammonia solution 10%	■	■	●	■	■	■	■	■	▲	■	■	■		●	■	■	▲	▲
Anone			■		■				▲	●	■				■	●		
Benzene	▲	■	■	▲	■	●		●	▲	●	●	●	●	▲	■	■		■
Benzine	●	■	■	▲	■	■	■	■	▲	●	●	■	■	■	■	■	■	

Common Tank / Tank Liner Materials:

- Polypropylene (PP)



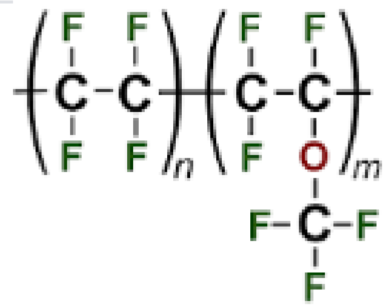




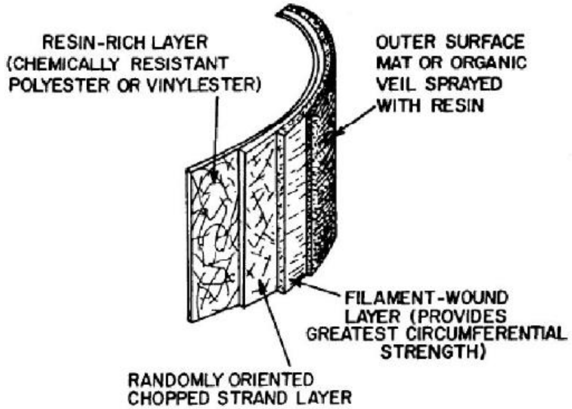
- Polytetrafluoroethylene (PTFE)

High Density Polyethylene (HDPE)

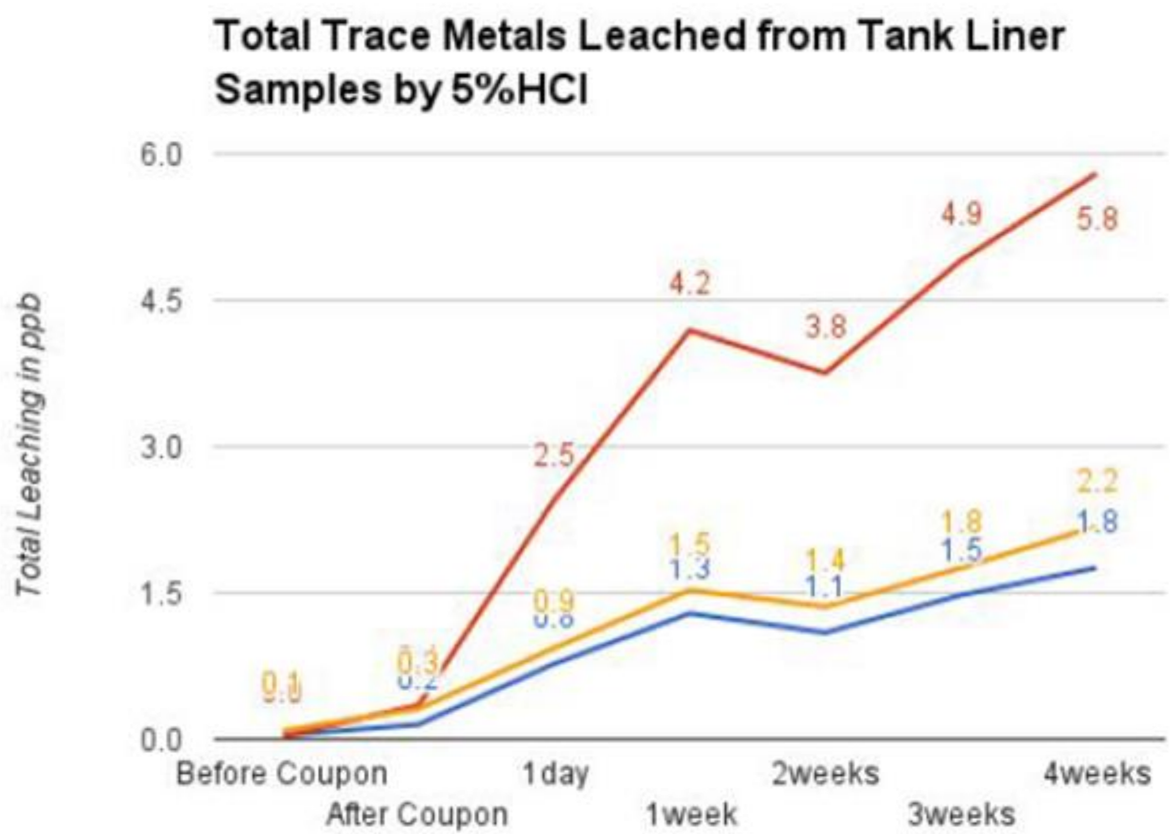
- PerfluoroAlkoxy



- FRP (Fiber Reinforced Plastic)



Leaching study of FRP Tank Coupons lined with three different “clean” polymers

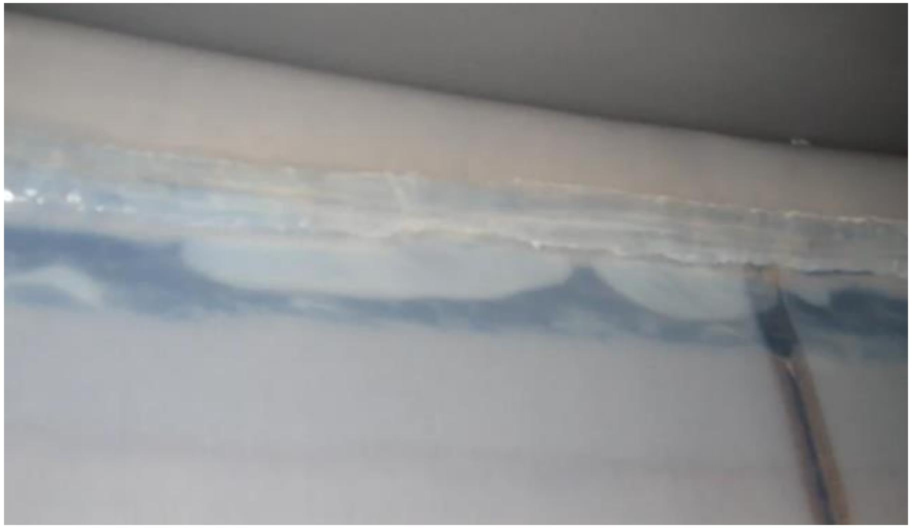


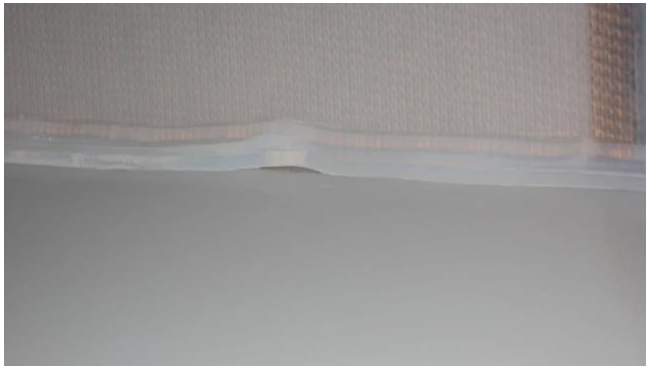
How the Heck did THAT Happen?

- CLNS tools using process Hydrogen Peroxide picked up large number of carbon particles as well as Na, Ca, Zn, K, and Mg.
  - From chemical supplier?
  - From Chemical Distribution System in the FAB?
  - From CLNS Tools?
  - Other?

Element	Filter/Syringe only	Tank wall material	Fiber sheets	
Li7(LR)	-0.001	0.473	0.385	ppb
Be9(LR)	0.004	0.005	0.005	ppb
Na23(LR)	2.539	67.975	368.413	ppb
Mo98(LR)	-0.009	0.049	0.02	ppb
Sb121(LR)	0.003	0.305	0.653	ppb
Ce140(LR)	0	0.005	0.011	ppb
Ta181(LR)	0	0	0	ppb
W184(LR)	0.001	0.039	0.041	ppb
Pb207(LR)	0.002	0.11	0.048	ppb
Bi209(LR)	-0.003	-0.002	-0.002	ppb
Mg24(MR)	6.403	6.215	58.831	ppb
Al27(MR)	0.22	17.503	11.511	ppb
Ca44(MR)	20.168	82.055	579.23	ppb
Ti48(MR)	0.144	1.555	5.689	ppb
V51(MR)	-0.002	0.09	0.742	ppb
Cr52(MR)	0.007	0.214	0.139	ppb
Mn55(MR	0.013	0.162	0.163	ppb
Fe56(MR)	0.025	0.803	1.149	ppb
Co59(MR)	-0.002	0.078	0.124	ppb
Ni60(MR)	0.086	0.174	0.125	ppb
Cu63(MR)	0.098	0.32	0.406	ppb
Ga69(MR)	0.001	0.001	0.003	ppb
Ge72(MR)	0.008	0.008	0.005	ppb
Sr88(MR)	0.016	1.041	1.076	ppb
Y89(MR)	-0.005	-0.004	-0.003	ppb
Zr90(MR)	-0.002	0.038	0.781	ppb
Nb93(MR)	-0.003	0.002	0.007	ppb
Cd114(MR	0.003	0.016	0.012	ppb
In115(MR	-0.006	-0.005	-0.005	ppb
Sn118(MR	0.004	0.01	0.164	ppb
Ba138(MR	0.006	0.152	0.271	ppb
La139(MR	-0.006	-0.005	-0.001	ppb
Hf178(MR	0	0.001	0.018	ppb
K39(HR)	2.174	21.984	37.312	ppb
Zn66(HR)	60.874	11.134	21.426	ppb

Poor workmanship in welded seams of inner PFA lining…..allowed chemical to infiltrate FRP and bring back ions and particles……





Why do chemical suppliers have detrimental particles?

- Many have been in business for decades and use the same process they used 50 years ago. They often use the same technology and often the same equipment they used when their factory was new!
- Some sources of particles include:
  - Incoming raw materials
  - Incoming water
  - Incoming air
  - "Cleanroom" manufacturing conditions
  - Shedding by process equipment
  - Handling
  - Transportation
  - Storage tanks
  - Infrastructure (pipes, valves, etc.)

Philosophies of Particle Reduction:

- Change the process and enhance process controls and monitoring
  - Often expensive
  - Makes suppliers nervous since it may adversely affect other customers not needing the level of cleanliness we do.
  - May have been running the same process for years, or decades, and any change is against their culture

Steps of Control Process

- Add lines of defense either within or at the end of the process just prior to shipment or at incoming to GF. (i.e., filtering)

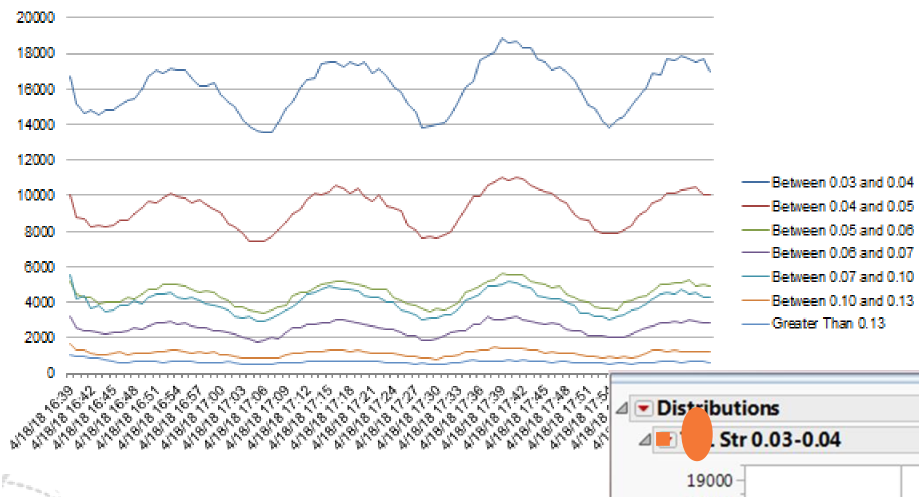
Specific Particle Reduction Process Areas:

- Incoming raw materials
  - View CofA (certificate of analysis) not just from our supplier but from our supplier’s suppliers
  - Site visit to supplier’s supplier
- Incoming water
  - Ion exchange
  - Reverse Osmosis
  - NOT City water direct feed!
  - Heat Exchanger feeds?
- Incoming air
  - HEPA and ULPA filters for air added into process columns, etc. (Ex: HEPA filter on stripper column)
- “Cleanroom” manufacturing conditions
  - HEPA filters (Ex: Storage tank manufacturing)
  - N2 blankets over chemicals in storage tanks or opent to atomosphere?
- Shedding by process equipment (Ex: pumps, valves, etc)
- Handling
- Transportation (agitation through distance is generally not good)

Particle Size Measurement

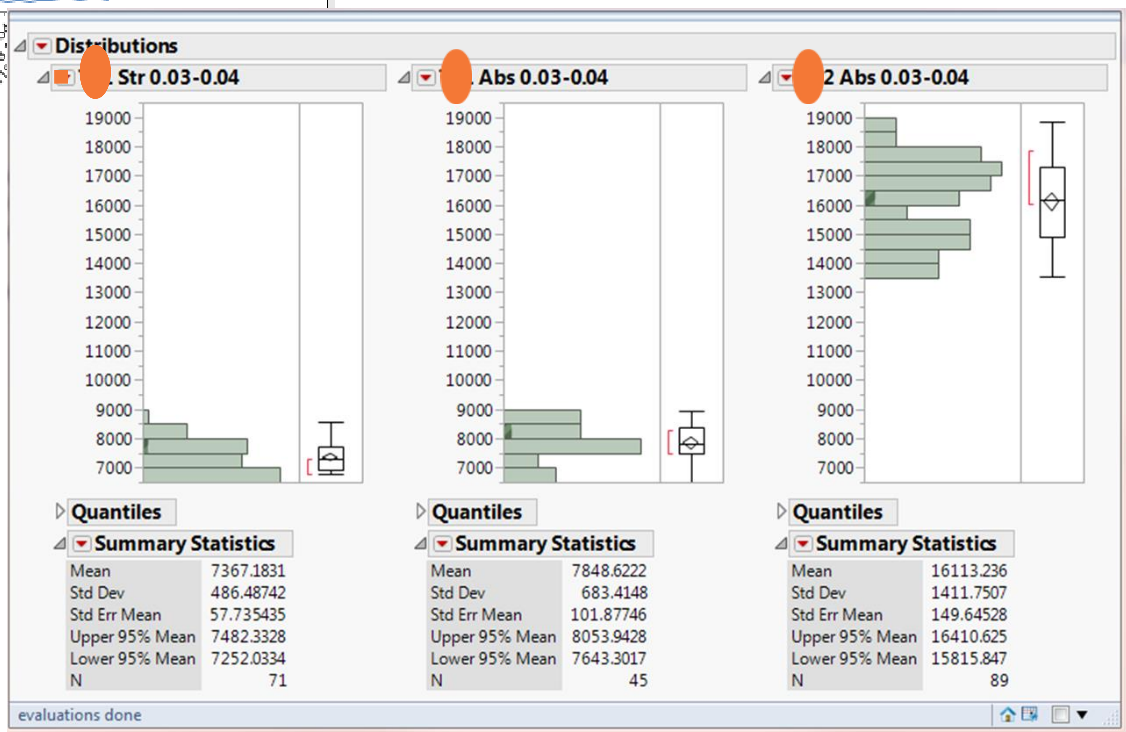
- **Techniques:**
  - **Optical**
    - **In line LPC (liquid particle counters)**
    - **Grab samples at control points**
    - **20-30nm bin size available with 10-15nm in development**
    - **Reputable manufacturers include RION, PMS, others**
  - **Acoustic**
    - **In-line Nanoparticle extractor, collector, and measurement**
    - **Claims to be able to measure down to 5nm**
    - **Not well accepted in the industry yet**
    - **Can it be made to handle non-aqueous chemicals?**

Raw data vs conditioned particle size data:



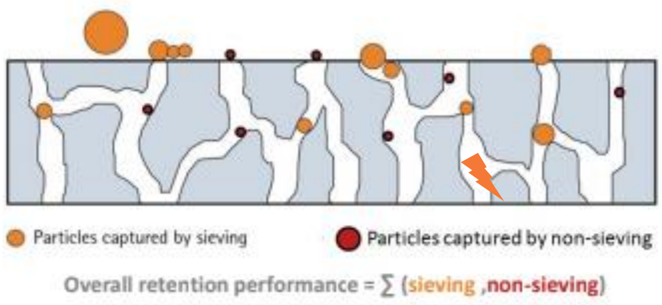
Raw data from RION LPC

LPC data analyzed and compared using JMP statistical software

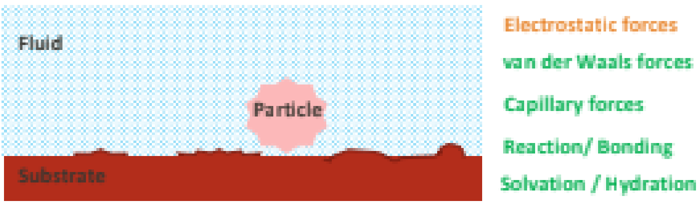


Mechanisms of Filtration

- Historic Depth Filters: Filtered through sieving



- New Membrane Filters: Filtered through sieving, tortuous path congestion, weak van der Walls forces, electrostatic forces, capillary forces between pore walls and particles

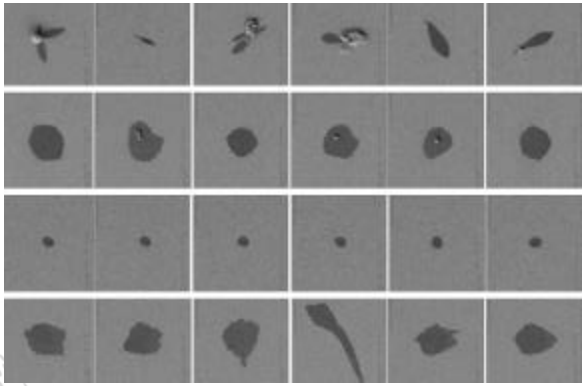


Diagrams courtesy of Entegris, from Ultrapure Micro 2018 conference, Austin, TX

When you want Effective Filtration……

1. Go with a reputable filter supplier who understands the science behind membrane filtration – not just a filter manufacturer or even worse, a distributor.
2. Make sure the filter material itself (membrane and support structure) is compatible with the chemical being filtered.

Example: HDPE (high density polyethylene) filter used for an n-butyl acetate based chemical and ended up depositing “particles” between 20nm and 200nm in size onto wafers, after passing through 5 nm POU (point of use) filters at the tools.



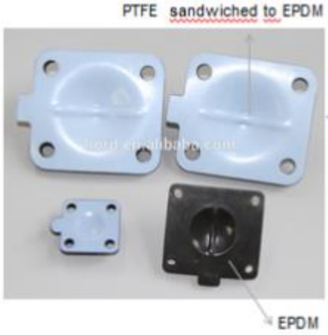
How the Heck did THAT happen?

Where did they come from?

How did they pass the tool filters?

Best Practices continued……

- Make sure infrastructure material (piping, valves, pumps, etc.) is compatible with the chemical
  - Example: 2018 – Sulfuric acid particulate excursion due to incompatible valve. Gasket made of EPDM (ethylene propylene diene monomer) which decomposed in contact with the acid.
  - Even if the hardware is not supposed to contact the chemical, something often seems to happen which causes this to occur.



- Materials Matter!
  - Polypropylene material is notoriously “dirty” and should not be used for high purity chemicals.
  - Polysulfone becomes brittle, breaks down, and sheds in peroxide and HCl.
  - PTFE and PFA are typically the cleanest, if the cost is acceptable ($5K vs $500).

Best Practices continued….

- Move to smaller pore size rated filter
  - Seems obvious, but not trivial. Pore size, efficiency, and retention ratings vary from supplier to supplier
  - Efficiency varies with particulate size, temperature, flow rate, and measurement scheme (measured with gold particles, latex spheres, alumina particles?) All will produce different "results", especially as the third method of filtration (electrostatic, van der Walls, forming monolayer on pore walls) becomes more important.

- Use PTFE or PFA diaphragm valves rather than valves with moving, rubbing parts (eg, ball valves) that generate friction and produce particles when operated.

Best Practices continued…..

- Where possible, use pre-washed, pre-wet filters
  - Filter material itself, whether hydrophilic or hydrophobic, will shed its own particles and metallics when first put into use.
  - Several reputable filter suppliers will offer pre-washed and pre-wet filters, sometimes with the same chemical you will be using, prior to shipping, and then vacuum pack the filter.
    - Sometimes difficult to ship the filter chemically “hot” if not aqueous based
  - Usually a little more expensive and needs more lead time to order
  - Prevents using your own production infrastructure to “clean” the filter
  - Be cautious of using hydrophilic pre-wash and wet if using to filter a hydrophobic chemical.
    - Very preliminary studies indicate the possible existence of leaving residual water in the filter or effectively eliminating some of the total usable surface area of the filter

Best Practices continued……

- **Don't "bump" the filters!**
  - Fast start up on a used filter can "undo" all the good the filter has been doing for the last six months! The monolayer can be disturbed.
  - Can variable speed motors, vfd's, "soft start" on pumps be used to slowly bring flow rates back up to operating conditions?
  - If the plan is to drain the system or go to full flow quickly, it might be a good idea to replace the used filter first, even though its lifetime has not been reached.
    - A new filter may cost $5K but how many wafers would need to be lost to justify a new pre-mature filter replacement?

Best Practices continued……

- **“Filter up” vs. “Filter down” orientation in the housing…..**
  - If a filter has it’s open side (gasket) down, and is removed for replacement, it is possible to drip “dirty” residual chemical into the output and contaminate the lines, especially if not sufficiently flushed prior to on-load and shipment.
  - Can also valve off initial flow after filter change so initial chemical flows to drain rather than to customer load.

- **Don’t “run to failure” on filters.**
  - Best practices is to routinely replace functional filters, usually on a pre-determined time basis. Some may change according to wafer count..
    - Depends on how clean the incoming chemical is
    - Change out frequency is usually determined empirically

Best Practices continued…..

- **Don’t wait for a differential pressure drop in order to decide that a filter is “plugged” and can begin shedding particles**
  - With the way membrane filters work today, a filter can be “spent” if depending on the third mechanism for filtration (monolayer formation) well before any noticeable pressure drop or decreased flow rate occurs, since cross sectional area of the pore has not been reduced.
  - A “spent” filter will begin to shed
    - Can shed old particles sinusoidally
    - Can allow new particles to pass through uninhibited.

- **If possible, install a new filter as soon as it is received.**
  - According to some reputable suppliers, filters do have a shelf life and lose efficiency and retention rate with time.
    - Some state that efficiency loss can begin in as little as a month if stored at room temperature.
    - Can increase shelf life through simple refrigeration?
    - Some suppliers indicate they are not aware of shelf life or degradation with time, but that may just mean they have not performed the experiments.

Best Practices continued……

- **When installing the filter, all handling should be "clean".**
  - Never use bare hands nor gloves coated with talc or anything else….
  - Filter supplier should recommend the procedure for cleanly changing out a filter
  - Some suppliers have engineered methods to avoid handling the filter completely other than with the sterile bag that it came in.
    - Example: Entegris has a quarter turn locking mechanism making it extremely easy to lock in a new filter using it's containment bag, avoiding contamination

- **Do not allow incoming pressure to exceed 40-50 psi for membrane filters, without supporting data.**
    - Can cause damage to the membrane itself
    - Can prevent particles from weakly adhering to the pore walls.
    - Increasing operating pressure on a used filter can cause shedding as well

Best Practices continued…..

- **Make sure you have the correct “O ring” for the chemicals being filtered.**
  - Kalrez? Viton? The material matters!
  - Check compatibility charts from the filter supplier and from additional sources (readily available on the web).
    - May even try some leaching experiments yourself!

- **Pre-wash or flush all filters in-house prior to use, regardless of what the supplier says.**
  - Can flush in actual operations loop or off line
    - Beware of handling issues if done off line
  - It’s your FAB (and your wafers)! - Not the supplier’s!

Filtration System Options:

Typical Need: Load 3000 gal of 96% H_2SO_4 in 2-4 hr time period at Temp = 25C with 50 psi at final filtration point = 47-95 l/min

Hypothetical Goal: Reduce 30-40 nm particles count to less than 1000 particles/ml as measured after final supplier filtration

Flow rate needs to be (750 – 1500 gal/hr) = (2839 – 5678 l/hr) =

(12.5 – 25 gal/min)= **(47 – 95 l/min)**

Suppliers: Modeling was done showing filter bank design needed to meet above conditions, along with CAPEX and Cost of Ownership. (Have multiple suppliers run models on same inputs to determine manifold configuration and corresponding dP)

Get capital cost with installation and total cost of ownership estimate

Supplier Capital Costs (ROM):

	15nm	20nm	30nm
Filter Supplier #1	**$65K**	**N/A**	**$60K**
Filter Supplier #2	**$72K**	**$56K**	**$65K**

Does not include design and installation costs and additional fitting costs

Cost of Ownership Model :

- Assumptions:
  - Housing lifetimes are 15 yrs (typical)
  - Filter lifetimes are 1 or 2 yrs (very dependent on how clean the material is)
  - Liters of sulfuric filtered annually in model: 500L, 1ML, 2ML, 4ML, 6ML

◦ **Total amortized cost based on annual consumption of H2SO4**

Annual Consumption	0.5 Ml		1.0 Ml		2.0 Ml		4.0 Ml		6.0 Ml	
Lifetime	1yr	2yr	1yr	2yr	1yr	2yr	1yr	2yr	1yr	2yr
30nm	$0.099	$0.0508	$0.0497	$0.0254	$0.0248	$0.0127	$0.0124	$0.0063	$0.0083	$0.0042
20nm	$0.081	$0.0414	$0.0403	$0.0207	$0.0201	$0.0103	$0.0101	$0.0052	$0.0067	$0.0034
15nm	$0.113	$0.0575	$0.0564	$0.0288	$0.0282	$0.0144	$0.0141	$0.0072	$0.0094	$0.0048

High Volume Magnetic Drive pumps at suppliers…..

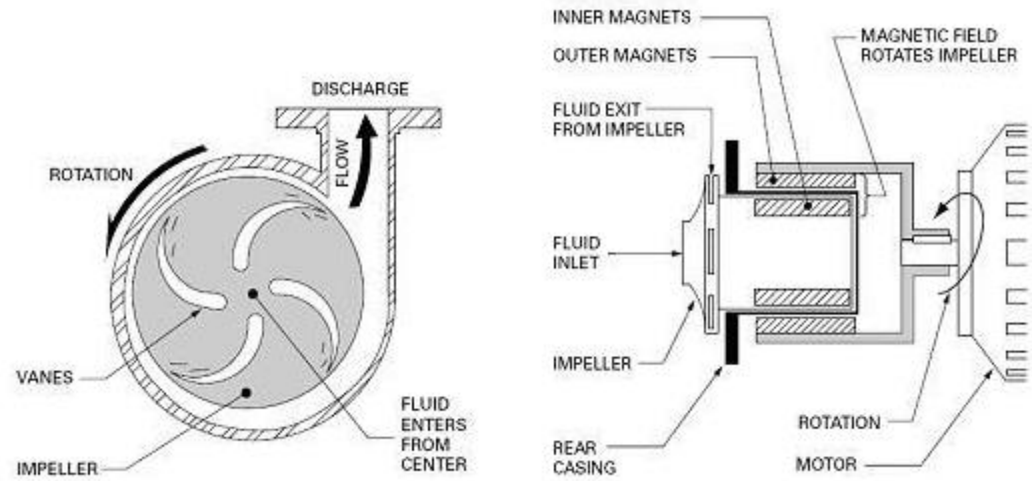


FIGURE 1: PUMP LIQUID END

FIGURE 2: PUMP MAGNETIC DRIVE

Possible significant chemical excursions due to failing mag drive pumps at suppliers, which would heavily contaminate supply, tools, and wafers…..

- failed SiC thrust collar
- failed SiC bearing
- failed SiC keyway
- routine pump change

How you protect against this?

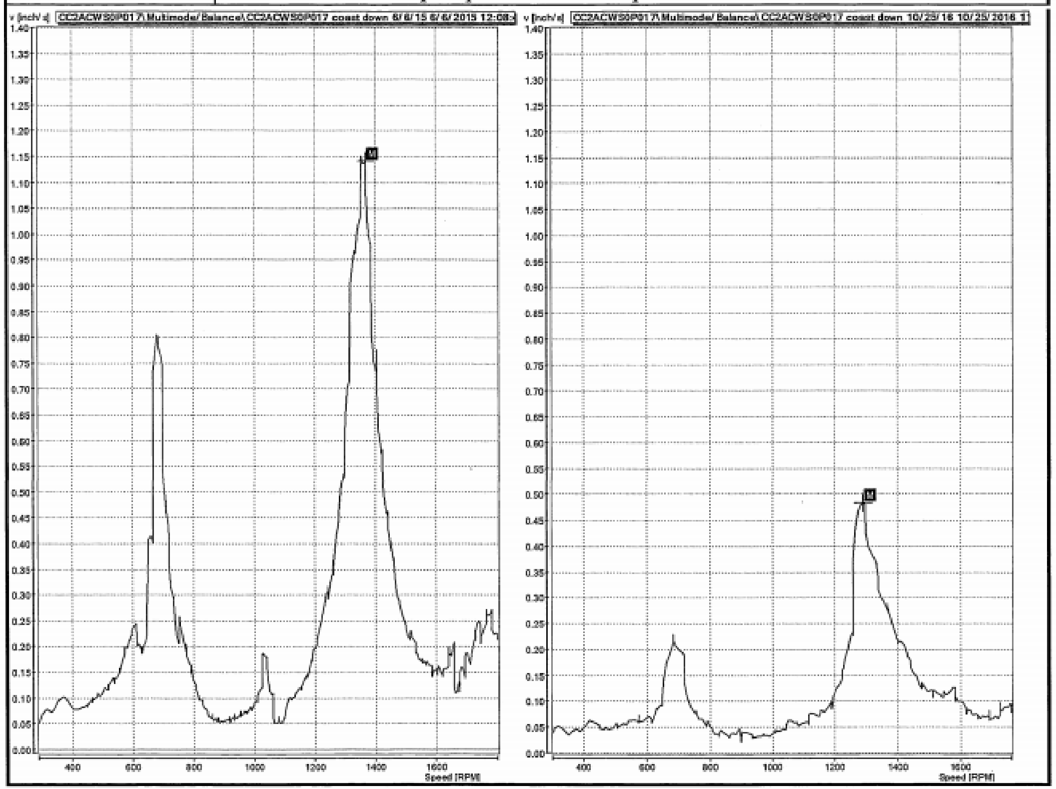
- increased filtration after pump
- vibration monitoring of pumps

Accelerometers mounted on pumps…..

- Mount accelerometers on pump and motor side in horizontal, vertical, and axial directions.
- Can be directly mounted if casing is magnetic and hard to reach or magnetic plate epoxied onto surface
- Can be wired to control box or Rf signal measured
- Can pick up multiple changes in pump operation, at motor, impeller failure, bearing failure, collar failure, cavitation, etc.
- Comparison is made to known good output, either supplied by manufacturer or measured directly by the user.
- Entire capital cost of < $10K if measured during rounds and readings with hand held units and portable accelerometers
- Some of our chemical suppliers who have had excursions are moving forward with this suggestion.

Pump vibration before and after replacing a failed pump…..

Name	Description
Coastdown before-after	overall vibration check based on operating speed. Data points were taken from 1800 RPM down to 300 RPM. Data shows significant decrease in vibration after new pump wet end was installed. Resonance still present but does not inhibit the pump from normal operation.



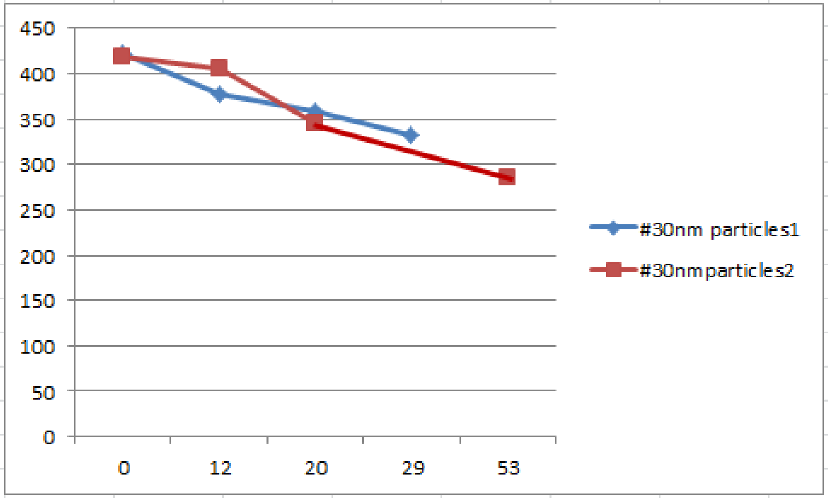
Does “in house” polishing help?

- Supply loop polishing using <= 50nm filters, once chemical is off loaded form ISOtainers.
- How long do we have to polish to make a difference? Do we reach an aymptotic limit where more polishing is useless?

	#30nm particles1	#30nmparticles2
0	423	419
12	377	406
20	359	346
29	332	
53		286

Linear reduction in #particles 30nm size over time:
3-11% decrease after 12 hrs
15-17% decrease after 20 hrs
22-28% decrease after 29 hrs
32-41% decrease after 53 hrs
No asymtotic limit appears to have been reached

"Dirty" Sulfuric - 30 nm bin



GLOBALFOUNDRIES Strategy with our Chemical Suppliers: **Help them Help Us!**

- Rather than just auditing them, our cross functional engineering team works with them to help solve their problems.
  - They often don't have the staff nor the expertise to solve issues found in audits
  - Trust levels are very low when we first reach out, but build as they see we are truly there to help them.
  - Sometime capital is involved, and that may need to be shared up front or in incremental costs during subsequent orders. Sometimes, they are just happy to solve their issues and pay for changes themselves.
  - It takes time to find the issues and engineer a solution, and get them to implement the suggested changes
  - We are careful to only make suggestions. Final decisions are theirs to own.
  - Are we helping them help others as well (our competitors?) Perhaps, but it is worth it for us to not be impacted.
  - This sometimes has financial implications for GF, but we believe it is worth it in the end to help them help us and prevent excursions and supply line issues.

Successes….

- With those suppliers with whom we have engaged….
  - They have agreed to evaluate, and implement in some cases, tighter filtration requirements, which should lead to tighter specifications at minimal increased cost
  - We are moving from unhelpful particle size specifications in a 14nm nm FAB to a more useful sub-30nm particle specification as enhanced filtration and process monitoring (in-line LPC’s) are implemented
  - Pump monitoring using accelerometers is occurring at multiple suppliers to prevent excursions
  - They better understand the output of their processes
  - Supply line issues are being avoided.
  - Trust has been established and we have been invited in to see the actual process in their operations as they see we are there to help.