

CLEAN MANUFACTURING

SEMICONDUCTORS

Fluoropolymers

survive acidic

environments,

but extractables must

be examined.

High Purity Acid Handling

Fluoropolymers

For several years many companies that process or utilize high purity acids in the semiconductor industry have settled upon fluoropolymers as a material of construction to ensure that limited amounts of impurities could be leached into the acids.¹

Fluoropolymers offer an advantage over other polymers since they are often manufactured in such a manner that no foreign additives that later could become extractables are needed for processing stability.² Fluoropolymers have advantages over metal in that they are not subject to chemical change (oxidation, rouging, etc.) and hence, will not have greater particle generation over time. In other words, a fluoropolymer's greatest period of leaching is the initial week of installation whereas a metal will become a greater source of leachate over time.^{3, 4}

A large number of case histories (tens of thousands) exist in the general chemical industry for the use of polyvinylidene fluoride (PVDF, PVF2), polytetrafluoroethylene (PTFE), and perfluoroalkoxy (PFA) resins. These materials of construction have many applications in strong acids even at high temperatures, and as long as they are used within the manufacturer's recommended temperature ranges for the named chemical, these resins have proven success for over 25 years.^{5,6,7,8,9}

With all of this history, answering the question as to whether the polymer will stand up to a chemical and temperature environment is easy. The less obvious part of the equation is whether the fluoropolymer could be adding extractables to high purity versions of semicon-

ductor-grade acids? For example, it is well proven in deionized water testing that a polymer simply maintaining its physical properties in exposure to water does not necessarily qualify it as a fluid handling component for high purity application due to extractables that can be emitted as high as part per million (ppm) levels.¹⁰

High Purity Acid Testing: HNO₃, HF, H₂SO₄, HCl

Data generated on extractables in this study involved high purity water (ionic extractions), HNO₃ (70%), HF (49%), H₂SO₄ (96% and 20%), and HCl (37% and 30%). Other extractable data in acid has been generated on fluoropolymers and published in earlier works.¹¹ Due to the permeation effect of polarity of the polymer and chemical being tested for extraction, the aggressiveness of a particular acid for certain elements, and the molecular size of an acid molecule plus additional water in its composition, it was thought to test four different acids to best develop a cross section of data.

The fluoropolymers selected were emulsion type PVDF (hereafter referred to as E-PVDF) and a designated specific high purity (HP) version of PFA (hereafter referred to as HP-PFA). Both of these polymers are commonly used by professionals in the above acids in general chemical containment as well as in high purity applications.

Table 1. Leachable Anions by IC.

Leachable Anions	Detection Limit (DL) ppb (ug/L)	HP-PFA Resin ppb (ug/L)	E-PVDF Resin ppb (ug/L)
F ⁻	0.1	*	*
Cl ⁻	0.02	*	*
NO ₂ ⁻	0.02	0.10	0.08
Br ⁻	0.02	*	*
NO ₃ ⁻	0.02	*	*
HPO ₄ ⁻	0.02	*	*
SO ₄ ⁻	0.05	*	*
Total Extractions	NA	0.10	0.08

*Nothing detected

NA-Not applicable

Table 2. Leachable cations by IC.

Leachable Cations	Detection Limit (DL) ppb (ug/L)	HP-PFA Resin ppb (ug/L)	E-PVDF Resin ppb (ug/L)
Li ⁺	0.01	*	*
Na ⁺	0.01	0.02	*
NH ₄ ⁺	0.05	0.16	0.07
K ⁺	0.02	*	*
Total Extractions	NA	0.18	0.07

*Nothing detected

NA-Not applicable

Table 3. TOC measurements in HF and H₂SO₄.

Acid Exposure	Detection Limit (DL)	Control Blank TOC (ppm)	HP-PFA Resin TOC (ppm)	E-PVDF Resin TOC (ppm)
49% HF	0.1 ppm	0.2	0.4	0.3
96% H ₂ SO ₄	0.2 ppm	*	0.5	0.5
20% H ₂ SO ₄	0.2 ppm	*	*	*

*Nothing detected

Test Methods: IC, ICP-MS, TOC

The scope of this data generation was to compare resins in their raw form to negate the effects of processing. Since processing could be largely dependent on the quality and cleanliness of a manufacturer, pellets were used in the corresponding method of extraction. The authors thought it could be unfair to represent sticks of tubing from one PVDF processor and one PFA processor when there are several established processors of each resin type commercially promoting the product lines. Designers should be cautioned that the same resin molded or extruded by different processors could have widely different results depending on handling techniques utilized by the processor.¹²

The test methods used to provide data were:

- ▶ **Ion Chromatography (IC):** leachable ions and leachable anions in high purity water
- ▶ **Inductively Coupled Plasma/Mass Spectroscopy (ICP-**

MS): leachable elements in high purity acids.

- ▶ **Total Oxidizable Carbon (TOC):** TOC measured from acid exposure.

Extraction Results and Discussion

▶ **Water Testing.** More than 20 years of data exists on PVDF and PFA in water.^{13, 14} The water industry has settled, that for rigid piping and components, PVDF is more than suitable to handle 18 megohm/cm water and is typically chosen over PFA due to strength considerations and overall costs.^{15, 16, 17} **Tables 1 and 2** list IC results for leachable anions and leachable cations from 100 ml of ultrapure water at ambient conditions in exposure of 1 gram of pre-cleaned HP-PFA and E-PVDF for 7 days. The results are given in ppb (ug/L) and in neither case were extractables even near 1 ppb for any ion tested.

▶ **Acid Testing.** TOC extractions are a consideration for high purity acid in that while bacteria typically will not survive in strong acidic environments, TOCs themselves added to the acid from fluid handling components act as system contaminants. TOC measurements were generated after 7 days exposure to 49% HF, 96% H₂SO₄ and 20% H₂SO₄ at ambient temperature. The results are listed in **Table 3**. Since the control blank measurement in HF was above the detection limit, it is appropriate to consider actual extractions from the tested resin to be less than the measured value. PFA and PVDF TOC extractable results were in the part per billion range.

ICP-MS was used to determine the extractable contributions of HP-PFA and the emulsion PVDF resin in contact with strong acids for 50 elements for 7 days at room temperature. The data was generated by using 1 gram of polymer to 150 grams of chemical. Extraction results are presented in **Tables 4, 5, 6, 7**. No data is listed for the control blanks for each chemical because the laboratory reported only a few measured leachables attributed to the blanks (0.1 ppb Al in the 37% HCl blank; 1.0 ppb Al and 0.2 Na 96% H₂SO₄ blank).

Discussion of Results

The testing in acids by IC, ICP-MS, and TOC confirm, in a test with a high ratio of contact surface to liquid volume, that both the PFA grade tested and the PVDF grade tested yield extractables below the part per million level in total cumulative leachate. TOC was the highest contributor of measured extractions for the three acids tested.

PFA does not change color in long term acid exposure and has gained wide use based on the above performance and the aesthetic nature of the color stability attributed to this resin. The E-PVDF (ASTM D3222, Type I, Class 1 and 2) used in this test does not substantially change color over time when exposed to this set of acids. Some commercial PVDF resins do change color substantially when exposed to concentrated hydrochloric acid, concentrated sulfuric acid and even water over time and this has created industry

Table 4. ICP-MS Leachable for 50 elements in 70% HNO₃ immersion

Element	Detection Limit Leach ppb (ng/g)	HP-PFA Leach 70% HNO ₃ ppb (ng/g)	E-PVDF Leach 70% HNO ₃ ppb (ng/g)
Al	0.1	2.5	6.9
Ba	0.05	0.5	2.7
Ca	3	95	7.5
Cr	0.1	0.9	0.2
Co	0.05	0.2	*
Cu	0.1	3.7	2.8
Fe	2	6.8	6.6
Pb	0.1	0.4	*
Mg	0.1	5.7	1.2
Mn	0.1	0.3	0.1
Mo	0.05	0.05	*
Ni	0.05	2.9	0.3
K	3	8.5	*
Na	0.1	40	110
Sr	0.05	0.6	0.09
Sn	0.05	0.1	0.1
W	0.2	*	5.6
Zn	0.5	3.0	1.5
Total Cumulative Leachate Measured	NA	131.15	145.59

Nothing detectedNA-Not applicable***Table 6.** ICP-MS leachable for 50 elements in 49% HF immersion.

Element	Detection Limit ppb (ng/g)	HP-PFA Leach 49% HF ppb (ng/g)	E-PVDF Leach 49% HF ppb (ng/g)
Al	0.1	4.9	7.7
Ba	0.05	0.3	2.4
Ca	3	13	5.8
Cr	0.1	1	0.3
Co	0.05	0.5	*
Cu	0.1	2.7	2.5
Fe	2	8.8	11
Pb	0.1	0.3	*
Mg	0.1	9.1	1.6
Mn	0.1	0.3	0.2
Mo	0.05	0.3	0.06
Ni	0.1	2.7	0.4
K	3	9.9	*
Na	0.1	48	100
Sr	0.05	0.3	0.07
Sn	0.05	0.2	0.2
Tl	1	3.8	2.4
Zn	1	2.9	1.6
Total Cumulative Leachate	NA	109.00	136.23

Nothing detectedNA-Not applicable*

caution in specifying the less expensive PVDF fluoropolymer for use in some high purity facilities. The scope of this study did not include extraction tests on such color sensitive suspension type PVDF (ASTM D3222 Type II) resins.

Throughout the testing, the elements detected from each resin were consistent. In no case were the following elements detected in this test: Sb, As, Be, Bi, B, Li, Hg, Nb, Pd, Pt, Rh,

Table 5. ICP-MS Leachable for 50 elements in 37 and 30% HCl immersion.

Element	Detection Limit ppb (ng/g)	HP-PFA	HP-PFA	E-PVDF	E-PVDF
		Leach 37% HCl ppb (ng/g)	Leach 30% HCl ppb (ng/g)	Leach 37% HCl ppb (ng/g)	Leach 30% HCl ppb (ng/g)
Al	0.1	2.5	2.3	4.4	5.3
Ba	0.05	0.3	0.3	2.4	2.8
Ca	3	37	47	7.1	6.3
Cr	0.1	1.2	1.1	0.5	0.3
Co	0.05	0.2	0.3	0.2	0.1
Cu	0.1	7.1	7.5	1.5	2.1
Fe	2	9.6	8.0	4.5	6.4
Pb	0.1	0.8	0.6	*	0.3
Mg	0.1	6.0	7.2	0.8	0.5
Mn	0.1	0.2	0.3	*	*
Mo	0.1	0.2	0.2	0.3	*
Ni	0.1	2.7	2.8	1.2	0.5
K	3	10	8.0	*	*
Na	0.1	36	31	28	81
Sr	0.05	0.3	0.6	0.06	0.07
Sn	0.1	0.2	0.2	0.3	0.2
Zn	1	4.0	3.0	*	1.3
Total Cumulative Leachate Measured	NA	118.30	120.40	51.26	107.17

Nothing detectedNA-Not applicable*

Rb, Ru, Sc, Se, Si, Ag, Ta, Tl, Th, U, V, and Zr. In most cases, calcium was the largest leachate contributor from HP-PFA, followed by sodium and potassium. In all cases, sodium was the largest leachate contributor from E-PVDF and usually calcium was the second highest contributor.

Nitric acid seemed to be the most effective extractive media for both resins, but none of the acids were able to extract above 150 ppb elemental leachate from either fluoropolymer in any test. In analyzing this data at such a minute level, the reviewer must understand that these extractions are typically non-exact. For example, at this level of sensitivity, 0.3 ppb and 0.1 ppb are essentially the same number and within limits of error. One would not say that one product is three times better than the other, but with enough data, trends can be determined as to the frequency expectations of finding various elements in any

Table 7. ICP-MS leachable for 50 elements in 96% and 20% H₂SO₄ immersion.

Element	Detection Limit ppb (ng/g)	HP-PFA	HP-PFA	E-PVDF	E-PVDF
		Leach 96% H ₂ SO ₄ ppb (ng/g)	Leach 20% H ₂ SO ₄ ppb (ng/g)	Leach 96% H ₂ SO ₄ ppb (ng/g)	Leach 20% H ₂ SO ₄ ppb (ng/g)
Al	0.1	2.4(a)	1.8	3.3(a)	2.4
Ba	0.05	0.4	0.1	2.2	1.0
Ca	3	16	31	5.1	5.4
Co	0.05	0.3	0.2	*	*
Cu	0.5	4.0	2.2	0.8	0.8
Fe	2	17	15	3.4	3.8
Pb	0.1	0.4	0.2	*	*
Mg	0.1	4.8	2.7	0.6	0.4
Mn	0.1	0.3	0.2	*	*
Ni	0.1	1.4	1.1	*	0.2
K	3	10	11	*	*
Na	0.1	26	25	23	18
Sr	0.05	0.1	0.2	0.06	*
Ti	1	1.5	*	1.2	*
Zn	0.5	3.9	3.6	1.1	0.8
Total Cumulative Leachate	NA	88.50	94.30	40.76	32.80

*Nothing detected
(a) 1 ppb detected in blank

NA-Not applicable

tested polymer. In other words, the data developed in this study does not appear to suggest that either resin is largely superior to the other in any of the test acids, but perhaps the data will help in understanding what can be looked for when attributing low level extractables to these two fluoropolymers.

Historical testing and conventional wisdom support that continued testing on the same samples would lead to lower extractions each time a new rinse is performed. This is a great advantage of the use of plastics for high purity fluid handling. The plastic materials only contain a finite amount of entrapped extractables and because the materials are not subjected to a corrosion rate as would be typical for a metallic product, the extractions do not increase or have unpredictable changes over time.¹⁸

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