



Results of the ISMI Fluorinated Heat Transfer Fluids Survey

International SEMATECH Manufacturing Initiative
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Technology Transfer #09065014A-TR
International SEMATECH Manufacturing Initiative
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Abstract: This report from the ESHT001 project presents the results of a fluorinated heat transfer fluids survey of International SEMATECH Manufacturing Initiative (ISMI) and Semiconductor Industry Association (SIA) members. The purpose was to gather data on the use, volatility, purchase and waste tracking, and status of emission measurements of fluorinated heat transfer fluids. Results of other surveys in this series collecting technical data on greenhouse gases are in Technology Transfers #09065012A-TR and #09065015A-TR.

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Authors: Walter Worth

Approvals: Steve Trammell, Project Manager
Ron Remke, Program Manager
Joe Draina, Director
Laurie Modrey, Technology Transfer Team Leader

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1 EXECUTIVE SUMMARY

In support of the industry response to the U.S. Environmental Protection Agency (EPA) proposed mandatory greenhouse gas (GHG) reporting rule, the International SEMATECH Manufacturing Initiative (ISMI) Environment, Safety, and Health Technology Center was asked to develop surveys, collect survey responses, and analyze data for ISMI and Semiconductor Industry Association (SIA) members. A total of three surveys were conducted. Responses have been collected independent of the SIA to preserve respondent confidentiality. Reported herein are results of a survey on the use, volatility (i.e., vapor pressure at room temperature), purchase and waste tracking, and status of emissions measurements of fluorinated heat transfer fluids.

Fourteen companies participated, providing 37 separate responses.

Results showed that the semiconductor industry uses at least 17 different fluorinated heat transfer fluids with ambient vapor pressures ranging from 6 to 30,000+ Pascals. Four fluids may be candidates for exemption from the proposed regulation due to their exceptionally low vapor pressure.

The fluids are mostly used in closed-loop chillers for processes such as etch, chemical vapor deposition (CVD), implant, and device testing.

Most companies do not quantitatively track usage, recycling, and disposal of these fluids. Only two companies track the quantity of fluids lost in spills and leaks, and four track the quantity of fluids recycled or disposed off site. Off-site disposal usually consists of high temperature incineration or fuel blending. Currently, one company has tested for traces of these fluids in fab air, finding that concentrations are below 5 ppb.

2 SURVEY OVERVIEW

The survey asked the following questions:

- Do you operate processes that use fluorinated heat transfer fluids? If so, which ones do you use?
- What is the name of the process?
- What is the vapor pressure of each fluorinated heat transfer fluid?
- Are spills, leaks, material recycling, and waste disposal being tracked to complete a mass balance for the fluorinated heat transfer fluids used?
- Has fab air sampling been done? If so, what were the results?

3 RESULTS

Fourteen companies participated in the survey, providing data for 37 separate responses (two of them overseas). Based on the survey, the fluorinated heat transfer fluids are almost exclusively used in point-of-use (POU) chillers for etch, CVD, implant, and automatic testing. A few companies mentioned that in some isolated cases these fluids are used for resist stripping (wet tool), chamber cleaning, and leak testing. One respondent that uses the fluorinated heat transfer fluids in a process abates emissions with the house thermal oxidizer.

Table 1 lists the fluorinated heat transfer fluids used and their corresponding vapor pressures in Pascals (Pa) and psia. 3M and Solvay Solexis are the main suppliers of the fluids. Based on the survey, the most popular are marked by a pound sign (#). The vapor pressures range from a low of 6 Pa to a high of 30,324 Pa. However, one company reported vapor pressures ranging from 800–55,000 Pa, with the most widely used compounds in the 800–2000 Pa range. The vapor pressure of water was included in the table for comparison only.

Table 1 Names of Heat Transfer Fluids Used and Their Vapor Pressures

Heat Transfer Fluid	Vapor Pressure @ 20–25°C	
	Pascals	psia
Name		
3M Fluorinert FC 40 # &	400	0.058
3M Fluorinert FC 77 #	5,600	0.81
3M Fluorinert FC 3283 #	1,867	0.27
3M HFE 7100 #	26,931	3.90
3M HFE 7200 #	14,532	2.10
3M HFE 7300	5,585	0.81
3M HFE 7500 &	6	0.0009
*Galden HT – 70 #	18,798	2.72
*Galden HT - 90	13,332	1.93
*Galden HT – 110 #	2,266	0.33
*Galden HT – 200 &	<133	0.019
DuPont HFC - 134a **	655,405	95
ZT - 130	NA	
ZT – 180 &	266	0.0386
*Galden D02 - TS	NA	
*Galden D02 - TSX	NA	
*Galden PFS 2	30,324	4.39
<i>WATER (for comparison only)</i>	2493	0.36

* offered by Solvay Solexis

** liquefied gas with boiling point of -26.5°C

most popular fluids based on number of survey responses

& recommend exclusion from regulation due to very low vapor pressure

One company pointed out that the Global Warming Potentials (GWPs) of fluorinated heat transfer fluids range from 55–9,400, whereas an EPA report published in 2006 (EPA 430-R-06-901) states that the GWPs range from >6,000–9,000.

Most fluorinated heat transfer fluid use is associated with the replacement of electrostatic chucks (ESCs), which are cooled directly by the fluorinated heat transfer fluid. When the tool is opened and the ESC removed, some fluorinated heat transfer fluid is “lost” and later replaced by topping off the chiller reservoir. The “lost” material is collected either separately or, more typically, blended with other mixed solvent waste. Then, the solvent waste is shipped off site for incineration or use as fuel in cement production. In most cases, spills are wiped up and the “solvent”-contaminated wipes are collected in covered waste cans as hazardous waste and sent off site for high temperature thermal oxidation (i.e., incineration); however, the quantity of the waste is not tracked.

Most companies have records for only purchases of fluorinated heat transfer fluids. Just two companies track the quantity of fluids lost in spills and leaks. Four companies track the quantity of fluids recycled or disposed off site. None of the companies seem to attempt a comprehensive mass balance for the fluids.

One company provided data from airborne emission measurements (Appendix A), which detected fluorinated heat transfer fluids in very low concentrations in the air of several different semiconductor manufacturing fabs. Twenty-one samples were collected and analyzed by thermal desorption followed by gas chromatography and mass spectrometry. The concentrations ranged from about 1–99 ng/L (in the form of fluoroalkyl ethers). Using the ideal gas law to convert from ng/L to ppb shows that the calculated air concentrations for these measurements are all below 5 ppb.

Using the data for several commonly used fluorinated heat transfer fluids, a calculation was made to estimate how quickly these fluids would evaporate after a spill or leak (Appendix B). A 4 ft² spill 1/8 inch deep would contain about 4.68 pounds of fluid. To evaporate that much material would take 1 to 94 hours, depending on the molecular weight and vapor pressure of the fluid. If one assumes that a leak of that size would not go unnoticed in a 3-hour period, given the cleanliness of semiconductor manufacturing fabs, the whole spill would go unnoticed and ultimately evaporate if only one fluid spilled.

4 CONCLUSIONS

The survey of 37 responses from 14 companies showed that the semiconductor industry uses at least 17 different fluorinated heat transfer fluids with ambient vapor pressures ranging from 6 to 30,000+ Pascals. Four of the fluids reported have exceptionally low (<400 Pa) vapor pressures.

The fluids are mostly used in closed-loop chillers for processes such as etch, CVD, implant, and device testing.

The majority of companies do not quantitatively track usage, recycling, and disposal of these fluids. Currently only two companies track the quantity of fluids lost in spills and leaks, and only four companies track the quantity of fluids recycled or disposed off site. Off-site disposal usually consists of high temperature incineration or fuel blending.

So far, just one company has tested for traces of these fluids in fab air, finding that concentrations are below 5 ppb.

Appendix A –Testing Fab Air Samples for the Presence of Hydrocarbons

In 2006, one U.S. semiconductor manufacturing company tested several fabs for air contaminants, including traces of fluorinated hydrocarbons.

A.1 Sampling and Analysis

The sampling and analysis consisted of the following. Pumps set at a preset flow rate of 100 mL/min. pulled fab air through stainless steel tubes packed with multiple beds of proprietary adsorbents. The air was typically sampled in three locations in the fab over a 23-hour period.

After sampling, the sealed tubes were shipped to an analytical laboratory where they were analyzed by thermal desorption followed by gas chromatography and mass spectrometry. The test method was designed to analyze for semi-organic compounds in the n-heptane (boiling range ~100°C) to n-octacosane (boiling range ~430°C) range. Each compound detected was identified by a search of a Wiley library of 275,000 mass spectra or, when no matches were found, by the analyst's interpretation or best estimate of the most probable compound or class of compounds.

A.2 Results

Table A-1 summarizes the relevant results identified as fluoroalkyl ethers. The typical spectrum for each sample contains many more compounds that were not fluorinated. The organic compounds are classified into three boiling ranges: low boiling (C7–C10), medium boiling (>C10–C20, and high boiling (>C20). The values are shown here as supporting evidence of the presence of larger molecules that may originate from the fluorinated heat transfer fluids.

A.3 Conclusion

As can be seen from Table A-1, the concentration of fluoroalkyl ethers in the air ranged from <0.1 to 99.8 ng/L.

If one assumes that in 2006 the air make-up rate in a typical fab was 200,000 scfm, then the quantity of fluorinated heat transfer fluids lost in the fab exhaust air is approximately 700 lbs/yr for a worst case concentration of 5 ppb. This would be 10% of the ~7000 lbs/year (based on 500 gallons) of fluorinated heat transfer fluids that the EPA estimates a typical fab loses in a year (EPA 430-R-06-901).

A.4 Sample Calculations

The data in Table A-1 indicate that the highest concentration detected was 99.8 ng/L (say 100 ng/L). This can be converted to ppb as follows: $100 \text{ ng} \times 0.08206 \text{ (atm} \times \text{L)} / (\text{moles} \times \text{°K}) \times 296\text{K} / (1.0 \text{ atm} \times 500 \text{ g/mole}) = 4.9 \text{ ng/g}$ or ppb.

If one assumes the air make-up rate for a typical fab is 200,000 scfm and, in turn, that much air is exhausted from the fab carrying 4.9 ppb of fluoroalkyl ether emissions, the loss of fluorinated hydrocarbons to the atmosphere can be calculated as follows: $4.9 \text{ ppb} \times 200,000 \text{ scfm} \times 500 \text{ lbs/lbmole} \times 60 / (1\text{E}+09 \times 359 \text{ ft}^3/\text{lbmole}) = 0.082 \text{ lbs/hr}$ or 717 lbs/year.

Table A-1 Air Samples Taken in High Volume Manufacturing Fabs in 2006

Sample #	Concentration			
	Fluoroalkyl ether ng/L	C7-C10 ng/L	>C10-C20 ng/L	>C20 ng/L
1	4.8	39.5	39	1.4
2	61.6	57.6	23.4	0.7
3	99.8	74.7	23.6	0.6
4	24.7	42.1	4.9	0.5
5	16.3	15.0	4.1	<0.1
6	18	16.3	3.8	0.2
7	56.7	43.7	5.3	0.1
8	1.8	19.3	19.4	0.9
9	1.2	13.3	11.5	1.4
10	1.0	20.2	17.8	1.5
11	1.2	23.7	17.8	1.7
12	<0.1	2.0	0.8	0.1
13	<0.1	8.5	6.4	0.4
14	29	34.3	10.8	0.6
15	24.1			
16	35.4			
17	22.9			
18	15.5			

Appendix B – Estimate of the Time to Evaporate a 4 ft² by 1/8" Deep Spill

B.1 Conclusions

- A spill of 4 ft² × 1/8" deep = 4.68 lbs (assumed density of 1.8 g/cc).¹
- The amount evaporated in 3 hours ranges from 0.15 to 13.47 lbs for these commonly used fluorinated heat transfer fluids.
- The time to evaporate a 4 ft² spill ranges from 1 to 94 hours, depending on the vapor pressure and molecular weight of the fluid.
- Since the POU chillers that use fluorinated heat transfer fluids have closed systems, it is reasonable to assume such spills are rare.
- A 4 ft² spill would most likely be discovered and cleaned up in 3 hours.

Table B-1 Estimate of the Time to Evaporate a 4 ft² by 1/8" Deep Spill

Heat Transfer Fluid	MW lb/lb-mole	Mass Transfer Co. K (feet/sec)	Surface Area (ft ²)	Vapor Press. (psia)	Ideal Gas Constant (psi-ft ² /R/lb-mole)	Temp. (° R)	Est. Evaporation (lbs/hr)	Evaporation in 3 hours (lbs)	Time to Evaporate 4ft ² Spill (hrs)
FC-77	415*	0.0016	4	0.81	10.73	529	1.36	4.08	3.4
FC-3283	521*	0.0014	4	0.27	10.73	529	0.50	1.50	9.4
HT-70	410*	0.0016	4	2.7	10.73	529	4.49	13.47	1.0
HT-110	580*	0.0014	4	0.33	10.73	529	0.68	2.04	6.9
HT-200	870*	0.0012	4	0.019	10.73	529	0.05	0.15	93.6

*(according to EPA Burton report 430-R-06-901)

¹ Sample calculation: 4ft² × 1/8" spill = 4 × 0.125/12 (ft³) × 28.32 (L/ft³) × 1000 (cc/L) × 1.8 (g/cc)/454 (g/lb) = 4.68 lbs.

**International SEMATECH Manufacturing Initiative
Technology Transfer
2706 Montopolis Drive
Austin, TX 78741**

**<http://ismi.sematech.org>
e-mail: info@sematech.org**