

USES AND EMISSIONS OF LIQUID PFC HEAT TRANSFER FLUIDS FROM THE ELECTRONICS SECTOR



Office of Air and Radiation
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1. 0 INTRODUCTION

This report presents the results of initial research on the uses of liquid perfluorinated compounds (PFCs) as heat transfer fluids (HTFs)—materials to manage heat—throughout the electronic sector. The information was obtained from searches of the Internet using the search engine provided by Google. The objective of the searches was four-fold:

- Identify major uses and suppliers of liquid PFCs employed as heat transfer fluids;
- Identify leading *users*—suppliers/manufacturers of equipment that employ liquid PFCs and manufacturers of devices, device assemblies, and electronic products, which included the consumer, industrial and military sectors;
- Identify published estimates of air emissions and trends of liquid PFCs employed as HTFs in the electronic sector; and
- Identify options for estimating emissions from the top emitting sources.

During the manufacture of semiconductor devices, HTFs serve as coolants in chillers, removing excess heat during many manufacturing processes. During semiconductor device testing, containers of HTFs are cooled or heated to a desired temperature into which the devices are immersed to test their integrity. In addition, when testing the function of devices, HTFs are used to remove the heat the devices generate while being tested. HTFs are also used to attach semiconductor devices to circuit boards via solder, which may be melted by the vapor of an HTF heated to its boiling point. HTFs may also serve to cool semiconductor devices and other devices or systems that generate high heat during operation.

The remainder of this report consists of seven additional sections. The next section, Section 2, describes the physical and chemical characteristics of liquid PFC HTFs for electronic manufacturing. Section 3 presents the history of liquid PFC uses in the electronics sector, which is followed, in Section 4, by detailed descriptions of the current uses, focusing on the quantities used and the factors that govern selection of HTFs. In Section 5, annual emissions are estimated for each use. Section 6 presents the distribution of sources (users of HTFs) in light of the current and evolving structure of the electronics sector. Section 7 describes three options for estimating emissions, based on the information obtained from this initial research. The last section proposes additional

work aimed at clarifying the distribution of sources, the relative proportions of HTF use among competing technologies as well as the modes and amounts of emissions from liquid PFC HTFs.

2.0 CHARACTERISTICS OF LIQUID PFCS

Tuma reported that for managing heat loads in the electronic sector, liquids are sought that have high dielectric strengths, acceptable thermal conductivities and are also inert and safe. Perfluorocarbon (PFCs) liquids possess these properties (Tuma, 2003). Among these liquids are fully fluorinated linear, branched or cyclic alkanes, ethers, tertiary amines and aminoethers, and mixtures thereof. The chemicals can be straight chains, branched or cyclic, or a combination thereof (such as alkylcycloaliphatic and cycloethers) and are saturated (i.e., free of ethylenic, acetylinic or aromatic unsaturated parts). The skeleton can include catenary oxygen, trivalent nitrogen heteroatoms, or both, providing stable links between fluorocarbon groups that preserve the inert character of the compound (3M, 1991). Also among the PFC liquids with the desired properties for the electronics sector are perfluoropolyethers and mixtures thereof (Solvay Solexis, 2004).¹

The searches revealed two global manufacturers of liquid PFC HTFs. Solvay Solexis offers the perfluoropolyethers (often as mixtures) under the trade name GaldenTM (e.g., GaldenTM HT-135) with a practical temperature range of -40°C to +120°C for use in chillers; other Galden fluids are useful at higher temperatures (e.g., DO2-TS, up to 160°C in thermal shock testing (TST) and LS/215 up to 215°C) (Solvay Solexis, 2004). 3M also offers, perfluoroalkanes, perfluoroethers and tertiary perfluoroamines under the trade names FluorinertTM (e.g., FluorinertTM FC-3283), with a practical temperature range of -40°C to +120°C for use in chillers; other Fluorinert fluids are useful at higher temperatures (e.g., FC-5320 is used in TST up to 160°C and FC-70 up to 215°C (3M, 2004). Galden and Fluorinert fluids have molecular weights between 350 to 820 g/mole. Occasionally Krytox, a product of DuPont, appeared in the searches as a heat transfer

¹ The molecular formulas for the simpler classes of fully-fluorinated compounds are: perfluoropolyethers, $\text{CF}_3\text{-(O-CF(CF}_3\text{)-CF}_2\text{)}_n\text{-(O-CF}_2\text{)}_m\text{-O-CF}_3$; perfluoroalkanes, $\text{C}_n\text{F}_{2n+2}$; perfluoroethers, $\text{C}_n\text{F}_{2n+1}\text{(O)C}_m\text{F}_{2m+1}$; perfluorocyclic ethers, $\text{C}_n\text{F}_{2n}\text{O}$; tertiary perfluoroamines, $\text{(C}_n\text{F}_{2n+1}\text{)}_3\text{N}$. In these compounds, $n > 6$ and $m > 2-3$. FC-72, for example, consists mostly of C_6F_{14} with a boiling point of 56°C, while FC-75 is mixture of C_8F_{18} and $\text{c-C}_8\text{F}_{16}\text{O}$ with a boiling point of 102°C.

fluid. However, according to DuPont product literature, Krytox fluids, while being a perfluoropolyether (like Galden), serve only lubricant markets (DuPont, 2004). The molecular weights of Krytox fluids are high— between 1177 and 6034 g/mole, consistent with Krytox being lubricants (oils and greases) not heat transfer fluids (DuPont, 2004).

The dielectric properties and chemical inertness of Galden and Fluorinert liquids make them particularly attractive as heat transfer media in electronic fabrication, testing, assembly and operation. Their very high dielectric strengths and stable resistivity provide a dielectric barrier and reduce energy losses (i.e., stray currents) from the high fluctuating voltages and magnetic fields present in etching and CVD chamber environments. In addition, despite their relatively low thermal conductivities (compared to water), they possess other properties that make them useful HTFs, including, a wide range of boiling points, high densities, low viscosities, low pour points, low surface tension, and high thermal and chemical stability. Their compatibility with metals, plastics and elastomers makes these fluids attractive in thermal testing, reflow soldering as well as temperature control during device or system operation. They are odorless, nonflammable, nonexplosive, evaporate cleanly and are practically non-toxic, which results in easier safe usage and storage (Tuma, 2003).

Typical HTFs such as Galden and Fluorinert are encumbered by their relatively high vapor pressures, estimated long atmospheric lifetimes, and relatively strong absorbance of infra-red radiation, which indicates that, if not contained, their potential contribution to global warming is a concern. The few published reports indicate that the global warming potentials (GWPs) of liquid PFCs are similar to the gaseous PFCs used in semiconductor device and TFT-FPD (thin film transistor flat panel display) manufacture—emissions that are currently being controlled globally (see Table 1).

Table 1: PFC Gases and Liquids Used in the Manufacture, Testing and Operation of Electronic Components and Systems

Material	Gas ⁽¹⁾ /Liq., (Typical Boiling point, °C)	Molecular weight (Avg. for liquids)	Global Warming Potential (100 yr time horizon)	Source	Comment, GWP values
CF ₄	Gas	31	6500	SAR	
C ₂ F ₆	Gas	138	9200	SAR	
C ₃ F ₈	Gas	188	7000	SAR	
c-C ₄ F ₈	Gas	200	8700	SAR	
CHF ₃	Gas	70	11700	SAR	
NF ₃	Gas	71	8000	Molina et al, 1995	
SF ₆	Gas	146	23900	SAR	
FC-87	30	290	8900	T&T, 2001	TAR ⁽²⁾
FC-72	56	340	9000	T&T, 2001	TAR, C ₆ F ₁₄
HT-70	70	410	9000	T&T, 2001	TAR, C ₆ F ₁₄
FC-84	80	388	>6000	3M Data, 2004	T&K ⁽³⁾
HT-90	90	460	>6000	SS, 2004	T&K ⁽³⁾
FC-77	97	415	>6000	3M Data, 2004	T&K ⁽³⁾
FC-104	101	435	>6000	3M Data, 2004	T&K ⁽³⁾
FC-75	102	420	>6000	3M Data, 2004	T&K ⁽³⁾
HT-110	110	580	>6000	SS, 2004	T&K ⁽³⁾
FC-3283	128	521	8600	T&T, 2001	TAR ⁽²⁾
HT-135	135	610	>6000	SS, 2004	T&K ⁽³⁾
FC-40	155	650	>6000	3M, 2004	T&K ⁽³⁾
FC-5320	160	650	>6000	3M, 2004	T&K ⁽³⁾
HT-170	170	760	>6000	SS, 2004	T&K ⁽³⁾
FC-43	174	670	>6000	3M, 2004	T&K ⁽³⁾
HT-200	200	870	>6000	SS, 2004	T&K ⁽³⁾
FC-70	215	820	>6000	3M, 2004	T&K ⁽³⁾
FC-5312	215	820	>6000	3M, 2004	T&K ⁽³⁾

⁽¹⁾ Denotes properties at standard temperature and pressure. ⁽²⁾ It appears T&T have adopted methodology from Third Assessment Report to estimate certain GWP. ⁽³⁾ T&K denotes Tuma and Knoll, 2003, see reference 8 where T&K cite lifetimes of liquid PFC HTFs >2000 years to give GWP >6000 for 100-year integrated time horizon.

Recently, 3M and Solvay Solexis announced the availability of non-PFC heat transfer fluids with lower, although still significant, GWP values (T&T, 2001; Solvay Solexis, 2003). Examining these HTFs in detail, which have reported GWPs below approximately 400 and 3000 for the 3M and Solvay Solexis materials, respectively, is outside the scope of this report (for GWP estimates see Table 7.7 at http://www.grida.no/climate/ipcc_tar/wg1/pdf/TAR-06.PDF). Nevertheless, both 3M and Solvay Solexis claim to have lowered the atmospheric lifetimes and, therefore, GWPs without compromising the properties that make them attractive HTFs to the electronic

sector.² By virtue of judiciously substituting certain F-atoms with H-atoms within the fully fluorinated carbon compound, the lifetime is shortened via chemical reaction of the H-atoms with the ubiquitous atmospheric OH-radical.

3.0 HISTORY OF LIQUID PFC USE

PFCs have been and are applied to cooling electronics in evolving and expanding ways (Tuma, 2003). Heat is removed either by direct or indirect contact of the PFC liquid with the heat source, relying on either single or two phase modes of cooling, with the latter taking advantage of the latent heat of evaporation to remove more heat. In the early 1950s, liquid PFCs served as heat transfer media to cool sensitive military electronics, principally devices used in electronic countermeasure (ECM), radar, sonar, and guidance systems (Tuma, 2003). In the 1970s and 1980s, PFC fluids moved into commercial applications, initially for thermal testing and reflow soldering operations, and then to cool supercomputers, lasers, and x-ray targets (Tuma, 2003).

In the early 1970s, 65 percent of PFC fluids were used in thermal testing (which, replaced glycol/water mixtures) and 25 percent were used for cooling electronics in military systems. The remainder was presumably used to cool large transformers and power transmitter tubes, in competition with CFC-113 (Tuma, 2003).

In the 1990s, increasing semiconductor processing temperatures as well as the growing adoption of complementary-symmetry/metal-oxide semiconductor (CMOS) technology (which is adversely affected by higher temperatures) forced manufacturers to begin replacing deionized water/glycol fluids with liquid PFCs. Until then the DI/glycol fluids had been used exclusively in temperature control units (TCUs), units for regulating temperatures during etching, plasma enhanced chemical vapor deposition (PECVD), ion implantation, and photolithographic processes. In the latter 1990s, in anticipation of increasing semiconductor heat generation (from exponentially increasing transistor speeds and densities), semiconductor manufacturers initiated research on device spray

² 3M calls its substitutes segregated hydrofluoroethers, referring to the inclusion of a $-OC_nH_m$ (the H-containing) segment that is separated ("segregated") from the fully fluorinated segment. 3M trade names use HFE in the name. Solvay Solexis calls its substitutes hydrofluoropolyethers, referring to the substitution of H-atoms for the F-atoms on the terminating ends of the fluoropolyether. Further information for both supplies is available at www.solvaysolexis.com and <http://solutions.3m.com/wps/portal/s.155/97132>.

cooling with liquid PFCs in closed systems (Tuma, 2003). Hewlett Packard, for example, began exploring the utility of combining Fluorinert FC-72 and the nozzle-control offered by its inkjet technology (in a closed system) to spray-cool devices when and where cooling is needed (Hewlett Packard, 2002). During this period, Defense Advanced Research Projects Agency (DARPA) of the Department of Defense (DoD) and other DoD funding sources initiated programs to exploit the application of liquid PFCs to cool high-power electronics in military systems (SDA, 2000).

The initial transition from liquid water/glycol to liquid PFC cooling led to inadvertent increases in PFC emissions. Initially, device manufacturers typically replaced the water/glycol coolant with the liquid PFC, without any changes to the TCU pump, seals and connectors. The lower surface tension of liquid PFCs compared to water resulted in PFC loss via leakage, which equated to PFC atmospheric emissions. Current practice among semiconductor manufacturers is, when switching from water/glycol to liquid PFC TCU units, to replace pumps, seals and connectors to prevent leakages or to replace water/glycol TCUs with suitably designed PFC-using TCUs, which may or may not use lower-GWP HTF alternatives.²

In 2000, reports of new uses of liquid PFCs emerged. Exploration was initiated of liquid PFCs to cool rectifiers (which consist of high power isolated gate bipolar transistors for converting DC to AC current for electric motors) in hybrid vehicles.

By 2002, the predominant use of liquid PFCs had changed. Sales of PFC liquids for just TCUs for semiconductor manufacturing and testing approached 50 percent of all PFC heat transfer sales (Tuma, 2003).

By 2005, penetration of liquid PFC-usage reached applications in electronics manufacturing: (1) TCUs, (2) thermal shock testing (TST), (3), vapor phase reflow (VPR) soldering, (4) automatic test equipment (ATE), and (5) device cooling. The volume usages (%) corresponding to these five categories in 2005 were. 50 (TCU), 20 (TST), 10 (VPR soldering), 15 (ATE) and 5 (device cooling).³ (Werner, 2005).

³ Werner (2005) also reported that, in 2005, approximately 10% of the TCU usage employed low-GWP HTF fluids while the corresponding usage for ATE was 65%. Challenges are slowing the use of low-GWP alternatives TST and VPS applications.

This initial research provided information about commercial TCUs, thermal shock testing (TST), reflow soldering products, and cooling individual devices, clusters of devices, and commercial-off-the-shelf (COTS) assemblies. Consequently, the discussion of PFC-liquid use in these applications is the main focus for the remainder of this report.

4.0 EXISTING AND EMERGING USES OF LIQUID PFCS

Temperature control is of increasing importance during the fabrication, testing and operation of electronic *devices, products* and *systems*.⁴ As electronic components (or integrated circuits, ICs) and systems have advanced in speed, transistor density, and function, managing thermal budgets during fabrication has also increased. Testing device performance under expected temperature environments and providing for the dissipation of heat produced during device, product and system operation have also increased. Temperature regulation also determines the performance and reliability of surface-mounted devices (SMDs), where the electrical leads of numerous packaged IC devices and passive components (e.g., resistors) are interconnected by soldering, specifically a process called reflow soldering.⁵

Temperature control—the removal of excess heat by cooling—is achieved by air cooling and liquid cooling. Tuma & Tousignant (T&T) (2001) review the uses of liquid PFCs as heat transfer fluids. T&T as well as others indicate that liquid cooling is becoming the preferred method for dissipating the increasing amounts of heat associated with both device fabrication and shrinking electronics (cf. Simons, 1996). The reasoning is straightforward: the highest heat transfer coefficient for air (achieved through forced convection) is roughly $0.005\text{W}/\text{cm}^2/^\circ\text{C}$ compared to the corresponding figure for a

⁴ In this report the term electronic *devices, product* and *system* includes power and optoelectronic applications, such as metal oxide semiconductor-controlled thyristors and telecommunication cabinets. Power and optoelectronic applications are sources of growing revenues to the electronics industry.

⁵ The common method of soldering onto a substrate is by mounting devices on a preprinted substrate using a solder paste. The entire substrate is then heated, remelting the solder to interconnect the devices. This method of soldering is called “reflow soldering.” In 1999, reflow soldering equipment accounted for 78 percent of electronic soldering equipment sales and was projected to exceed 85 percent by 2006 (as reported in Fabtech at www.semiconductorfabtech.com/industry.news/005/10.08.shtml). A less common method is wave soldering, where a machine generated wave of molten solder alloy makes controlled contact with the devices being mounted. The surface mounting process may employ both reflow and waver soldering.

dielectric liquid (achieved via two-phase coolant spray) is $1.5 \text{ W/cm}^2/\text{°C}$, 300 times greater (Incopera and DeWitt, 1996).

PFC liquids, however, have long atmospheric lifetimes and high global warming potentials (T&T, 2001). Thus, to the extent they evaporate to the atmosphere, their contribution to global warming is a concern.

The remainder of this section summarizes four uses of PFC liquids: temperature control units used during the manufacturing process; integrated circuit (IC) testing; soldering to connect surface-mount devices; and cooling individual devices, clusters of devices, and commercial-off-the-shelf (COTS) assemblies.^{6,7} Each of these uses is described below.

4.1 Temperature Control Units (TCUs) For Manufacturing

Temperature control during IC fabrication is achieved through temperature control units (TCUs), part of the support equipment (such as vacuum pumps) attached to wafer cluster tools. TCUs use coolants to remove unwanted heat from wafers during film etching and deposition processes as well as ion implantation, and lithographic processes. Coolant is circulated through the wafer mounts during the process. TCUs are also used to remove heat from quartz windows and reactor domes. The semiconductor industry's continuous pursuit to reduce wafer processing costs (i.e., to lower the life-cycle cost of its equipment by considering equipment throughput, uptime, and effects on IC yield) is, among other things, motivating TCU design innovations, which facilitates switching from deionized water/glycol coolants to fluorocarbon liquids (Sheppard, 1999; BOC Edwards, 2004; Solid State Systems Cooling, 2003).

The available literature suggests that each process tool that requires temperature control has its own TCU (Sheppard, 1999; BOC Edwards, 2004). A modern 200 or 300 mm wafer fab will operate and maintain, respectively, approximately 1600 and 1400 distinct pieces of manufacturing equipment (Deutsche Bank, 2002; Smith Barney, 2004). In the

⁶ COTS electronics refers to military electronics and have lower maximum temperature ratings than the usual military specification. Conduction cooling, using dielectric liquids, is common in military electronics. (Wilson, 2003)

⁷ Because these uses of liquid PFCs occur in closed systems that are still limited to commercial and military systems (as opposed to the more ubiquitous consumer systems), the potential for significant amounts of direct air emissions appears less, although maintenance and disposal of systems cooled in this manner remains a potential concern.

300 mm wafer fab, approximately 10 percent of the equipment requires cooling; in a 200 mm wafer fab, approximately 8 percent of the equipment requires cooling and 10 percent for testing (Smith Barney, 2004). Product literature and other reports indicate that each TCU requires 1.5 to 50 gallons to fill, which presumably depends on heat loads (Solid State Cooling Systems, 2003; BOC Edwards, 2003; and Tuma and Knoll, 2003). Tuma and Knoll (2003) report that “by far the majority” of TCUs require approximately 8 to 50 gallons/system, with 5 gallons per system being typical.⁸

Table 2 summarizes the coolant used in the high-volume production of 200 and 300 mm wafer fabs, excluding “top-off”. The range for fab-coolant usage is large due to the limited knowledge of TCU coolant volume requirements (a factor of approximately 5) rather than limitations in knowledge about the number of tools that require TCUs. Coolant cost, which ranges from \$200 to \$500/gallon, is not insignificant—ranging from approximately \$38,000 to \$3,500,000 per fab, depending on assumed fab size, coolant capacity and coolant unit cost. However, coolant life is essentially infinite and never needs replacing if properly used, although some topping-off seems required every 1 to 2 years for a well-designed system (Tuma and Knoll, 2003).⁹

Table 2: Estimates of Liquid PFC Use for a 200 and 300 mm Production Fab That Uses Only Perfluorocarbons as Coolants in Temperature Control Units (TCUs)

Wafer size, mm	Number of TCUs ^a	TCU Coolant Capacity ^b , gal
200	125 units	188-6250
300	140 units	210-7000

^aAssumes one TCU for each PECVD, etch (dry), ion implant and stepper tool in fab.

^bAssumes a coolant capacity range of 1.5 to 50 gal/TCU; excludes “topping off” (Tuma and Knoll, 2003). Source: Smith Barney, 2004 for number of tools.

4.2 Automated Test Equipment and Thermal Shock Testing¹⁰

⁸ Later in this report there is discussion of the additional fluid volumes required to “top-off” TCUs due to leaks and evaporation in systems with “free-breathing” expansion reservoirs. These expansion reservoirs are designed to permit air saturated with the fluid vapor to leave the expansion reservoir as the fluid expands and contracts with each thermal cycle.

⁹ A brief, qualitative telephone survey of TCU equipment and HTF vendors by the author during July 2005 indicated that semiconductor manufacturers top-off TCUs at monthly intervals and that the top-off volumes appear to be decreasing as TCU designs are improving.

¹⁰ For convenience, automated test equipment and thermal shock testing are presented together in this report. However, the reader should be aware that HTF-usage in automated test equipment is rapidly transitioning from high-GWP to low-GWP fluids, which is more difficult for thermal shock

IC testing is undergoing transformation. Automated test equipment (ATE) accounted for approximately 10 percent of total capital equipment market in 2003 and 10 percent of the capital equipment cost of a new 300 mm wafer fab (Smith Barney, 2004). Recently, the Semiconductor Test Consortium revised the specification for the Open Semiconductor Test Architecture (OPENSTAR) to include air-cooling and liquid HTF cooling (www.semitest.org). HTF cooling improves thermal management during testing, providing for improved test stability and greater throughput when testing, for example, high-speed, large capacity memory devices (see www.advantest.com; see also www.amkor.com that also produces similar ATE). This initial research, however, did not produce information about the quantities of HTFs needed to fill or top-off these cooling systems. It appears, however, that the amounts would be similar to those for TCUs.

As ICs have continued to add functionality and speed in ever shrinking form (i.e., shape) factors, testing has grown more vital for ensuring design and manufacturing integrity. Thermal shock testing (TST) is an IC-screening test to discover defects that are attributed to differing coefficients of thermal expansion among materials (silicon, metals and dielectrics), which can result in IC or packaged-IC delamination during assembly or operation.

Component manufacturers or their subcontractors perform TST in one of two ways: (1) alternating hot and cold air; or (2) alternating hot and cold liquid. Manufacturers have considered liquid-to-liquid TST too expensive because, despite its proven effectiveness, replacing lost liquid—fluorocarbons—through evaporation is too high. However, recently TST equipment manufacturers have designed new chambers with fluid recovery features that lower fluid loss by up to 65 percent (ESPEC, 2004; Cincinnati Sub-Zero, 2003; ACS, 2003).

Liquid PFC use is more uncertain in TST than in TCUs. This initial research produced no information about (1) the proportion of fabs using air-to-air TST compared to liquid-liquid TST, (2) the proportion of fabs that outsource TST, and (3) testing protocols, which specifies the fraction of packaged die that require TST. Without this information, only

testing because of problems of material incompatibility between available low-GWP test-fluids and device packaging.

very rough estimates of liquid PFC use for testing at a typical fab can be made. Moreover, information was not found that either described or permitted estimates of the proportion of HTFs used in TST that are high-GWP fluids.³

A typical high-volume 300 mm wafer fab (30,000 wafer starts per month) requires approximately 150 tools to perform automatic testing of packaged components (Smith Barney, 2004). However, these tools are used for both electrical and thermal tests (i.e., thermal tests include both liquid-liquid TST and air-air equipment for TST).

The cost of PFC liquids for liquid-liquid TST appears to discourage this form of shock testing. Recent changes in test equipment designs, however, may favor the use of liquid-liquid over air-air TST because the duration of liquid-liquid test can be shortened. (More time is needed to bring the same mass of components to a fixed temperature (without overshoot) with air than with a liquid. Temperature uniformity throughout the packaged die also appears to be easier with liquids than with air.)

Consider liquid use at a 30,000 wafer start per month 300 mm wafer fab. At full production and commercial yields, this fab would produce approximately 13,000,000 to 15,000,000 die per month.¹¹ Not all of these packaged die would be tested. A sampling plan that specifies testing 10 die per wafer lot is roughly equivalent to sampling 0.1 percent of all die produced, or 13,000 – 15,000 packaged die per month in this example. If each packaged die weighs 5 g, then each month 65 – 75 kg of packaged die require testing. Commercially available liquid-liquid TST systems handle between approximately 1.5 – 3.5 kg of packaged die per TST test, with each test requiring between approximately 1 to 17 hours to complete (which includes loading and unloading the testing system), depending on the specific test (ACS, 2004; MEFAS, 2004).¹² If, for this example, only 17 hour tests are assumed to be performed, a fab could choose to have one or two 2kg or 3.5 kg TST systems, depending on its practices for tool utilization and system availability. If the lower (2 kg) capacity unit is chosen for this example, then

¹¹ In arriving at this range, a die of 110 m² is chosen together with reasonable assumptions about area for edge exclusions, defect densities, defect model and dies lost to test sites and alignment marks. The size of an MPU (microprocessor unit) is approximately 110 m² (Intel, 2004).

¹² Many protocols exist for liquid-liquid thermal shock testing, which are characterized by the number of cold-hot cycles per test and the dwell time at each temperature. The test protocol used in this example specifies 100 cycles, with hot and cold dwell times of 5 minutes each and transition period between each cycle less than 10 seconds. Other protocols may specify as few as 15 cycles and as many as 1000 cycles with longer or shorter dwell times (ESPEC, 1997; **ESPEC Technology Report: Evaluation Reliability**, Report No. 3).

approximately 650 hours (=38 tests x 17 hrs/test, or, 90 percent of available hours) of testing per month is required to shock test 75 kg of packaged die. A unit with 2 kg capacity requires 18 gallons of liquid PFC (for both baths that hold the packaged die) at a cost of \$3,700 to \$9,000, plus the cost to replace liquid lost via evaporation (Cincinnati Sub-Zero, 2004).¹³ ACS specifies evaporative loss rates of approximately 3 g/hour of testing for its 2 kg unit, so that over the course of a month, 1,950 grams of fluid is lost, or approximately 1 liter (the density of PFC liquids ranges between 1.6 - 1.9 kg/liter) for an additional cost of \$50 to 130/month (\$600 – 1600/yr). This estimate compares favorably to recent published reports by ESPEC for its newest design, which cite expected annual fluid replacements costs less than \$1,500/yr for its 2 kg system (ESPEC, 2004). The new systems from ACS, ESPEC, and CSZ use new designs aimed at significantly reducing evaporative losses. ESPEC reports that it has heard of annual fluid replacement costs as high as \$20,000 for older TST system designs, approximately 40 to 100 gal/yr (assuming a liquid PFC cost of \$200 to 500/gal). Depending on the capital cost of liquid-liquid TST units and the extent the claimed reduction in fluid loss is achieved, increased use of the liquid-liquid TST method may occur. However, a recent report touted Intel's purchase of a new kind of fast *air-air* shock testing system claiming significant increases in throughput (IRTS, 2003; Neves, 2003).

4.3 Vapor-Phase Reflow (VPR) Soldering

Reflow soldering is the principal soldering method to connect surface-mount devices (SMDs), multi-chip modules and hybrid components to circuit boards (CBs) in commercial, industrial, and military electronic products. Among the reflow soldering methods—simple air convection, forced-air convection, infrared, laser and vapor-phase reflow (VPR)—only VPR uses a heat transfer fluid. However, among the alternatives, the literature contains conflicting claims about the merits of each alternative. The principal encumbrance of vapor-phase reflow seems to be operating cost—machine maintenance, chemical cost and waste management requirements (Apell and Howell, 2003).

In vapor-phase reflow soldering, the melting (reflow) of the solder is achieved by placing the printed circuit board (PCB) with SMDs into a chamber with the heat transfer fluid,

¹³ Throughout this report reference is made to the cost of liquid PFC fluids. For convenience and consistency, the range \$200 to 500/gal is adopted (Tuma and Knoll, 2003).

heating the fluid to its boiling point (the melting point of the solder, 215°C for lead-containing solders and 20 to 35°C higher for lead-free solders), and then removing the SMD-PCB after gradual cool-down. The total time in the chamber is 3 to 5 minutes, depending on the mass and density of the SMD-PCB. Liquid PFCs serve as the HTFs. Both in-line (conveyor-belt handling) and batch-type systems are used, with the latter favored for mass-production (Intel, 1998; Concoat Limited, 2004). Device manufacturers provide instructions for surface mounting the devices they manufacture. For example, both Micron (memory products) and Altera (programmable logic devices) do not recommend vapor-phase reflow for surface mounting their devices, while Intel and Intersil do support vapor-phase reflow for surface mounting its products (MICRON, 2004; Altera, 2002; Intel, 2004; Intersil, 2004).

Quantification of the industry's use of VPR soldering compared to reflow alternatives that do not use liquid PFCs was not found during this initial research. Nor was information obtained regarding the share of HTFs represented by high-GWP fluids compared to the low-GWP substitutes.¹⁴

Robinson (2004) reported increasing interest in and opportunities for VPR because of the advent of lead-free soldering. He noted the virtues of VPR—less risk of overheating or device damage—but also cited its major hurdle was relatively low throughput (because of longer reflow time) and high liquid cost (Robinson, 2004). Nevertheless, some IC manufacturers, system assemblers, and manufacturers of soldering equipment promote the virtues of VPR soldering—for both lead and lead-free surface mount technologies (Intel, 2004; Intersil, 2004; Gregory and Liecht 2004; 3M, 1990 and 2004; Concoat, 2004).

An earlier study report provided by 3M (1990) seems to support the more recent claims of Gregory and Light (2004) and Robinson (2004). The 3M report, using information from a study conducted by Centech of Singapore in 1990, compared the device mounting cost per circuit board of four conveyORIZED (in-line) soldering machines: one VPR soldering, and three infrared-heated reflow soldering machines (3M, 1990). In the 3M report, the cost-performance of VPR soldering was superior. The total cost for surface mounting devices was \$0.0207/board, approximately 20 percent lower than the

¹⁴ See footnote 3, wherein it appears low-GWP fluids are not in use in VPR.

cost of the closest alternative. This and the reports of Gregory and Light (2004) and Robinson (2004) suggest that VPR is popular today, despite the emergence of other methods, which do not use expensive PFC liquids, such as forced convection heaters. Apell and Howell observe, however, that VPR is an all but forgotten technology—perhaps not as popular as it was in the 1970's and 1980's (Apell and Howell, 2003).

A substantial part of the cost of VPR soldering is fluid loss. The cost-performance for VPR reported by 3M (1990), for *in-line* machines included fluid loss. The FC-70 (Fluorinert, liquid PFC) loss rate was 0.12 lb/hr (54 g/hr) of use (3M, 1990). At an annual utilization rate of 80 percent (7,000 hrs per year) for the in-line soldering system, the annual liquid loss is 55 gallons, an annual cost of \$11,000 to \$28,000. The cost of this liquid loss contributed \$0.005 to \$0.01 to the total cost of surface device mounting (or, 23 to 48 percent of the total cost for surface-mount devices) (3M, 1990). Gregory and Leicht (2004) give a lower range for fluid loss rates for in-line systems, between 10 to 15 g/hr. For an assumed utilization of 7,000 hr/yr, the annual loss rate, using Gregory and Leicht's range, is between 10 and 15 gallons/yr, an annual cost of \$200 to \$7,500/yr. Gregory and Leicht also note that VPR is particularly well suited when using lead-free solder, currently being introduced by the electronics industry. In this instance, according to Gregory and Leicht (2004), it is simply a matter of using a different fluorocarbon heat transfer fluid, one that has a higher boiling point to reach the higher melting point of most lead-free solders.

Gregory and Leicht (2004) also provided a range for fluid loss from the use of *batch* VPR SMD systems. For batch systems, Gregory and Leicht give a loss rate of 5 to 10 g/hr, which, for 7,000 hr/year utilization, corresponds to 5 to 10 gal/yr of fluid loss, Gregory and Leicht do not indicate whether the lower range for fluid loss reflects the use of a secondary fluid above the primary liquid, which, according to 3M product application literature, reduces aerosol formation and vapor loss of the primary working fluid (3M, 2004).¹⁵ Regardless, Gregory and Leicht's is the only estimate of fluid loss from batch systems identified from this initial research.

¹⁵ For example, 3M offers a secondary perfluorocarbon fluid, SF-2, for use above the primary fluid. The thin vapor blanket formed by heating this fluid above the primary fluid helps to prevent aerosol formation and vapor loss of the primary liquid to the atmosphere.

As noted at the beginning of this section, this initial research neither resolved the extent of nor the prospects for VPR-soldering in device assembly.

4.4 Temperature Cooling Of Devices, Clusters Of Devices And Commercial-Off-The-Shelf (COTS) Assemblies

This section summarizes the apparently growing commercial and continuing military use of liquid PFCs for cooling high-power-density electronic systems. The literature in this area is vast, esoteric, and dense. However, while many techniques exist for cooling, in almost every situation, just two fundamental objectives drives cooling these high power systems: (1) prevent exceeding the critical device junction temperature (which, if exceeded either degrades performance¹⁶ or produces device failure), and (2) remain below the solder melting point (which, if exceeded produces system failure). The exception to these two objectives for cooling electronic systems applies to high-powered electric motors: their performance improves with liquid cooling compared to air cooling. For example, large electric motors vibrate less and operate more efficiently with liquid cooling compared to air cooling. Less vibration means quieter operation, an important result when the electric motors power submarines (Harris and Hildebrandt, 2003).

No information was obtained about the current or expected annual consumption of PFC liquids for high-power electronic-cooling applications. Neither was their information obtained that provided a means for estimating that consumption during operation. Thus, unlike the discussion of liquid PFC use in device fabrication, testing and assembly, the discussion that follows is more qualitative, providing little insight about the quantities of liquid PFCs used in cooling high-power electronic systems. However, for all of these applications, the liquid PFCs are used in closed (often hermetically sealed) modules, where losses would seem to be negligible except during maintenance and decommissioning.

For the purposes of this report, liquid-PFC cooling applications of high-power electronics are separated into consumer, commercial (non-consumer), and military applications. Furthermore, the only consumer application for liquid-PFC cooling of potential significance is assumed to be high-performance desktop computers. However, liquid cooling is not currently in use in mainstream consumer applications because, despite the

¹⁶ As junction temperature increases in semiconductor devices, switch times decrease; but at some upper temperature the devices fails.

ever increasing heat dissipation from advanced microprocessor chips and wireless RF (radio frequency) modules, new chip designs and innovations in thermal packaging continue to extend the life of conventional heat-sink-assisted air cooling (Bar-Cohen, Avram, 1999; Mukherjee, S. and Mudawar, S., 2002; CTS, 2004). Nevertheless, liquid cooling kits are sold, apparently, to the few users who operate microprocessors at higher voltages, which increase the processing speed (called “overclocking”) and heat generation of the PC, exceeding the off-the-shelf cooling capability. These kits use approximately 300 ml of either water or fluorocarbon coolant to remove the excess heat produced (see www.hexus.net.co.uk for a description of the product cooling method offered by Asetek called Waterchill). Liquid PFC use in this application is understandably preferable to water inside a PC. These after-market PC products do not provide guidance to prevent the release of the liquid-PFC to the atmosphere.¹⁷

The commercial liquid PFC applications category, as described earlier in this report, includes cooling of supercomputer, telecommunication and airport radar systems, which as described by Tuma (2003) and others (Simons, 1996; Bar-Cohen, 1999), is 1970-vintage technology. In these applications, bare packaged chips or modules of packaged chips are cooled by direct and indirect contact with liquid fluorocarbons. Boiling of the coolant at the exposed packaged surfaces provides high heat transfer, sufficient to meet chip cooling requirements. The PFC-containing enclosure possesses internal metal fins to provide the means to condense the vapors and remove heat from the liquid. Air-cooling of a cold-plate attached to the enclosure lowers the coolant temperature via attachment to a cold-plate. Other well known cooling concepts that use liquid PFCs and may be on the cusp of mainstream commercial applications are spray cooling, jet impingement, or pumpless pool boiling of fluorocarbon liquids directly onto the chip; these concepts provide the required heat transfer by combining a heat exchanger to condense the coolant for reuse (Bar-Cohen, 1999; Mukherjee and Mudawar, 2002; CTC, 2004). The designs of these cooling systems envisage a very long coolant life without replacement, and also provide environmentally sensitive instructions for decommissioning the system.

¹⁷ Other, more expensive approaches to cool overclocked PCs use elaborate refrigeration modules.

Cooling of high-power military systems with liquid PFCs will likely increase. Keltec (a Crane Aerospace company) recently announced a system that uses liquid PFCs for continuously cooling airborne and mobile high powered microwave assemblies and transmitters that is mounted on a metal plate through which coolant passes (see www.sigtech.com/keltec/products1.htm). Evidence also exists of several military R&D programs and the prospect for increased use of liquid cooling. Spray cooling, jet impingement cooling and pool boiling appear favored for future military systems. Isothermal Research Systems (ISR) seems to be the dominant if not the only enterprise doing commercial development work and shipping operational spray cooling systems to the military (www.spraycool.com; SDA, 2000). In all of these cooling applications, the liquid PFC appears to be contained in a reservoir from which it passes (pumped through a cold plate in the case of simple change of phase cooling, or nozzles in the case of spray and jet impingement cooling) to the chip-containing module. The vaporized PFC then passes through a heat exchanger where it condenses and returns to a reservoir after being purified by a filtration system. The life of the coolant matches the life of the electronic system, so no maintenance or coolant replacement appears required.

5.0 MAGNITUDE OF AIR EMISSIONS FROM THE USE OF LIQUID PFCs

This initial research identified four estimates of air emissions resulting from using liquid PFCs at semiconductor manufacturers. Additional information was obtained that permitted estimating emissions from cooling, testing, and reflow soldering processes that use liquid PFCs. The searches provided no emissions information for emissions from liquid PFCs associated with the operation and maintenance of electronic equipment. However, the information obtained during this initial research suggests, as previously noted, that emissions from cooling electronic equipment are smaller than other sources, albeit unquantifiable at this time.

5.1 PFC Emissions from HTF Use in Manufacturing ICs—Cooling and Testing

Of the four estimates for manufacturing, T&T provided an estimate for a typical but uncharacterized high-volume fab, vintage 1999-2000. Semiconductor manufacturers provided the other three estimates for their global operations (Seif and Hermanns, 2002; Seiko Epson, 2002; Mitsubishi, 2002). The estimates reported by semiconductor manufacturers do not explicitly identify the uses—cooling, testing and VPF soldering— included in their estimates.

T&T provide estimates of air emissions from “a typical high volume fab”. T&T do not specify the capacity (i.e., level of wafer production) for this “typical high volume fab”. The fab probably uses 200 mm wafers in light of the 1999 vintage. Neither does T&T specify the number of pieces and the nature of the equipment that comprise their estimate, i.e., T&T neither provide the proportion of equipment that performs cooling for etching, deposition, etc. processes nor the corresponding proportion that performs testing. T&T evidently combine the two functions and report that “during a year when no manufacturing capacity is being added”, the consumption of “virgin PFC liquid” is, on average, 500 gallons. Accepting the validity of this interpretation as well as T&T’s assumption to use of the properties of C₆F₁₄ (specifically the density and GWP of C₆F₁₄), these 500 gallons equate to 0.0079 million metric tons of carbon equivalent (MMTCE).¹⁸

T&T compare this estimate to the annual uncontrolled gaseous PFC emissions for a hypothetical 200 mm high volume fab (Beu and Brown, 2000), which was estimated by Beu and Brown using the Intergovernmental Panel on Climate Change (IPCC) Tier 2a, 2b and 2c emission estimation methods. T&T’s comparison shows that the air emissions from liquid PFC losses range between 17 to 19 percent of the total emissions during IC manufacture (i.e., use of gaseous and liquid PFCs), with the smaller figure corresponding to the Tier 2a method (Beu and Brown, 2000).

Seif and Hermanns (2002) presented the share of total global warming emissions from “topping off” liquid PFC in 2001 across AMD’s worldwide operations. While acknowledging several uncertainties in each component of the total (which is comprised of emissions from using energy, N₂O and gaseous and liquid PFCs), the authors estimate that 5 percent is the contribution from using liquid PFCs. Seif and Hermanns did not indicate what figure or figures were used for the GWPs of the liquid PFCs they use. AMD’s estimate can be restated in terms of the fraction of PFCs emitted from its facilities in 2001. The result is 15 percent for the share of AMD’s global emissions from all PFCs, i.e., from use of gaseous and liquid PFCs. This 15 percent figure is roughly

¹⁸ T&T use the properties of C₆F₁₄ to convert the 500 gallons/yr lost to 0.0079 MMTCE (= 500 gal x 3.7854 l/gal x 1.7 kg/l x 9,000 (GWP) x (12 C/44 CO₂)/10⁹ kg/MMT). The GWP for C₆F₁₄ from the Second Assessment Report is 7,400; the more recent estimate from the Third Assessment Report is 9,000, Table 10-8, p. 10-28 for 100-year time horizon. Substituting 7,400 for 9,000 would lower T&T’s estimate from 0.0079 to 0.0065 MMTCE. This adjustment is not made in this report.

comparable to the corresponding figures reported by T&T (2001) (Seif, and Hermanns, 2002).

Two other reports of liquid PFC emissions from semiconductor manufacturers were obtained from this initial research. Japanese semiconductor manufacturers publish annual environmental reports, which may include estimates of both gaseous and liquid PFC emissions. Not stated is whether the reported emissions for liquid PFC use include those for cooling and testing. However, they likely include both uses. Table 3 summarizes the available figures for Seiko Epson and Mitsubishi for the period 1997 – 2001. There are no references in the report as to how PFC emissions are estimated. It appears, however, that emissions of the gaseous PFCs used during IC manufacture rely on IPCC procedures and that emissions of liquid PFCs rely on estimates of annual liquid loss.

In reporting these figures, the companies appear to use the GWP of C_6F_{14} , as did T&T. Table 3 shows that over the 5-year period, emissions from both gaseous and liquid PFCs decreased. In the early years of 1997 and 1998, when emissions were practically unchanged and uncontrolled at Seiko Epson, the share of total emissions from the use of liquid PFCs was approximately 18 percent, close to the corresponding share estimated by T&T. For Mitsubishi, the corresponding fraction is 14 percent, closer to the corresponding figure reported by Seif and Hermann for AMD. In the later years, when manufacturers were reducing emissions associated with both gaseous and liquid PFCs, the shares of total PFC emissions from liquid PFCs decreased to as little as 5 percent for Seiko Epson.

Table 3: Reported Air Emissions from Use of Gaseous and Liquid PFC at Seiko Epson (A) and Mitsubishi (B) for 1997 – 2001 (10,000 Mtons, CO₂)

a. Seiko Epson

Type of Emissions	1997	1998	1999	2000	2001
Liquid PFCs	4.8	4.8	2.7	1.2	0.5
All PFCs emissions	26.8	27.4	36.3	21.7	9.9
Liquid PFCs, % of total	17.9	17.5	7.4	5.5	5.1
b. Mitsubishi					
Liquid PFCs	NA	NA	6.1	6.1	3.7
All PFCs emissions	NA	NA	44.9	49.1	40.8
Liquid PFCs, % of total	NA	NA	13.6	12.4	9.1

Sources: Seiko Epson, 2002 Environmental Report, p. 54; Mitsubishi, 2002 Environmental Sustainability Report, p. 35.

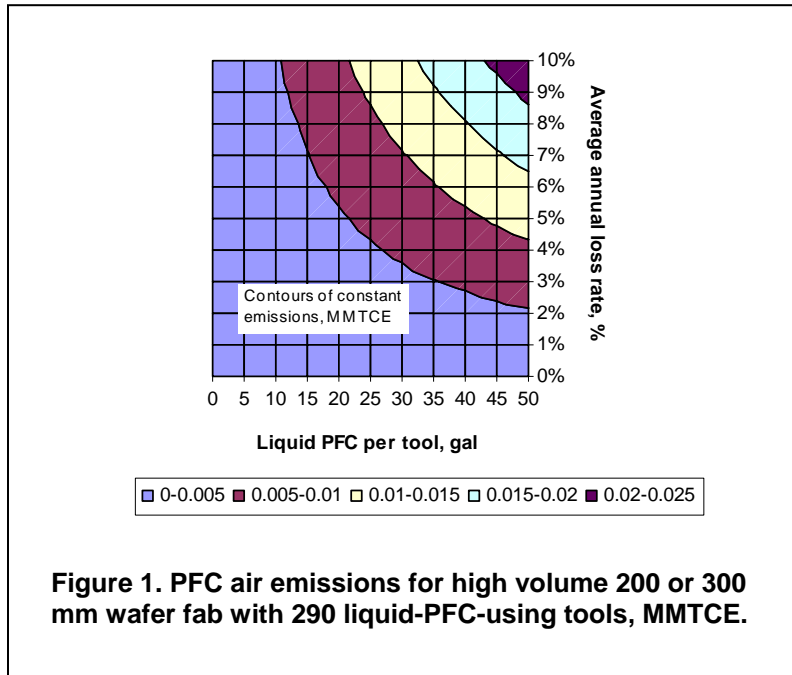
The estimates in Table 3 for uncontrolled emissions from using liquid PFC may also be compared to the absolute emissions estimated by T&T for the hypothetical fab. Converting the Seiko Epson emissions from liquid PFCs of 4.8×10^4 Mtons CO_2 to MMTCE units, gives 0.013 MMTCE or 1.6 times the 0.0079 MMTCE figure for T&T's single hypothetical high production fab. The corresponding 1999 figure for all of Mitsubishi operations is 0.016 MMTCE, or 2.1 times the T&T single-fab figure. These comparisons are not only consistent with the T&T's single fab (0.0079 MMTCE) estimate but are close to T&T's per fab estimate in light of the number of production fabs operated by Seiko Epson in 1999 and 2000 (see footnote 22).

These published estimates of uncontrolled emissions may also be compared to uncontrolled values calculated for a new high-volume 200 or 300 mm wafer fab, each with a capacity of 30,000 wafer starts per month. A 200 fab would need approximately 290 tools, of which 165 would be devoted to IC testing; the corresponding 300 mm wafer fab would need approximately the total same number of tools but fewer for testing—150 instead of 165 (cf. Table 2). Using the 290 estimate as the maximum number of tools that might use liquid PFCs together with the usage figures given in Table 2 and Tuma and Knoll's (2003) estimate that, on average, the annual loss rate is <10 percent, an estimated range of annual emissions from liquid PFC use can be developed. The equation use to estimate the annual emissions, Q, is:

$$Q(\lambda, T) = [290 \text{ tools } (12 \text{ C}/44 \text{ CO}_2) / 10^9 \text{ kg/MMT}] \sum_i \rho_i \text{ GWP}_i \lambda_i T_i = 79 \times 10^{-9} \rho \text{ GWP } \lambda T,$$

where for the purposes of these estimates, single (average) values replace the subscripted values with ρ , GWP, λ and T denoting, respectively, the density (at 1.7 kg/l), the global warming potential of C_6F_{14} (9,000), the average leak rate across all liquids (%/yr) and T is the average quantity of liquid required to initially fill the tools (liters). The quantities λ and T are treated as variables, allowed to vary over a reasonable range for each (Tuma and Knoll, 2003). In simplifying the formula, it is reasonably assumed that the quantities are uncorrelated.

The results are given in Figure 1, where lines of constant emissions (MMTCE) are shown. The



GWP for C_6F_{14} of 9,000 (SAR) is assumed for these calculations. If the emissions estimate from T&T (0.0079 MMTCE) is accepted as roughly correct (which may or may not include emissions from losses during testing), then, for an average liquid PFC per tool of 25 gal/tool, the results in Figure 1 show that an annual average loss rate over all tools that use liquid PFC falls between approximately 7 and 8 percent.

As previously mentioned in Section 4.2, the estimated annual liquid losses ranges between 3 to 100 gal/yr for semiconductor manufacturing. The lower amount is associated with newly designed low-loss TST equipment (ESPEC, 2004); the larger amount was estimated by dividing ESPEC's customer reports of the annual cost of liquid losses (\$20,000) by \$200/gal, the lowest reported cost of liquid PFCs for testing. This range in lost liquid becomes 0.00005 to 0.0016 MMTCE of air emissions, assuming the fluid density is 1.7 kg/l and GWP is 9,000 (C_6F_{14}).¹⁹ This range is consistent with T&T's estimate for liquid PFC loss of 0.0079 MMTCE.

¹⁹ The figure 0.0016 MMTCE = 100 gal/yr x 3.785 l/gal x 1.7 kg/l x 9,000 x (12 C/44 CO₂)/10⁹ kg/MMT. The figure 0.00005 MMTCE = (3 gal/100 gal) x 0.0016 MMTCE.

In Section 5.1, it was noted that T&T's estimate of 0.0079 MMTCE was likely to include emissions from both the losses from temperature control and testing equipment, although the portions were not provided. Using the range 0.0005 to 0.0016 MMTCE from testing, suggests that as much as 20 percent of T&T's estimate could include losses from testing ($= 0.0016/0.0079$). However, if T&T's estimates excludes emissions from testing, then T&T's estimate could be increased to 0.0095 MMTCE ($=0.0079 + 0.0016$). It should also be noted that the estimates for TST emissions, by definition, exclude HTF losses from ATE.

5.2 PFC Emissions from Vapor-Phase Reflow Soldering

This section considers emissions during VPR soldering, the arguably popular and only surface mounting technology among several that use liquid PFCs. Because no information about emissions from either assembly or product manufacturing facilities (which use VPR soldering) was obtained from the initial research, this section presents calculated estimates.

As shown next, such an estimate shows that if *all* packaged ICs from a high-volume wafer fab were assembled using VPR soldering, those emissions could equal 55 - 66 percent of emissions from using liquid PFCs in equipment cooling and device testing, or 8 – 11 percent of the total emissions associated with electronics manufacturing. Those emissions from VPR soldering, however, most likely occur at locations other than where the packaged ICs were manufactured and tested. The basis for this range is described next.

In the section on VPR soldering, a large range for liquid loss during soldering was presented—5 to 55 gallons per 7,000 hours of soldering. For the purposes of estimating annual loss from a facility that might use vapor-phase reflow, the results from the comparative study published by 3M are consistent and useful.

According to the 3M-published study, 55 gallons would be lost over the course of 7,000 hours. The published study also reported that 620 (7" x 6") boards were completed per hour. Over the course of the 7,000 hours, assuming approximately 7 mounted devices per board, 30,380,000 tested, packaged ICs would be soldered while losing, through

evaporation, 55 gallons of liquid PFCs.²⁰ Thus, approximately 5 - 6 similar soldering lines would be needed to surface-mount the annual quantity of packaged ICs produced at one modern high-volume wafer fab (e.g., 5.1 soldering lines = [13,000,000 ICs mounted/month x 12 month/yr]/[30,380,000 ICs mounted/year/soldering line]). Together these 5 - 6 lines would emit (each at 55 lost gallons/yr) the equivalent of 275 to 330 gallons of liquid PFCs. This volume equates to 55 - 66 percent of the emissions from liquid PFC loss that T&T estimated for a typical high volume fab (e.g., 330 gallons evaporated = 0.0052 MMTCE compared to T&T's estimate of 0.0079 MMTCE)²¹.

Table 4 summarizes estimates of PFC emissions associated with electronic manufacturing that were identified in or developed using information from this initial research

Table 4: Estimates of Uncontrolled PFC Emissions per High-Volume Electronics Manufacturing Facility

Emissions Mode	Estimate 1		Estimate 2		Source	Comment
	MMTCE	% of Total	MMTCE	% of Total		
Gaseous	0.039	76	0.039	72	Bue & Brown, 2000	Hypothetical, 1999 vintage hi-volume fab, IPCC Tier 2a method
Liquid (loss)						
Cooling, TCUs	0.0079	15	0.0079	15	Tuma & Tousignant, 2001	Typical 1999-2000 hi-volume fab, 500 gallons annual loss
Liquid-liquid shock	NA	NA	0.0016	3	This work	Only liquid-liquid testing done; 0.1 % of all packaged die tested
VPR Soldering	0.0043	8	0.0052	11	This work	All packaged products surface mounted using VPR soldering
Totals	0.051	100 ⁽³⁾	0.054	100 ⁽³⁾		

³ Totals may not sum to 100 because of rounding.

The estimates of emissions in Table 4 are initial estimates of *uncontrolled* emissions associated with electronics manufacturing. The estimates conceal many assumptions although those assumptions have been identified explicitly throughout this report. Those assumptions fall into two broad categories: (1) fab characteristics, such as technology vintage, capacity, utilization, wafer size, tool mix, heat management practices, die size, yield, sampling protocol, etc., and (2) HTF usage, such as the proportion and magnitude

²⁰ In this estimate, the number of mounted-devices per board is important. The figure 10 devices per board is similar to figures from Concoat, which reports that, for its vapor-phase reflow Delta-5 system, 48 devices are mounted on a 50 cm by 40 cm board or roughly 2.4 devices per 100 cm² area of substrate (cf. 7.70 cm² or 2.6 per 100 cm² in this estimate).

²¹ 0.0052 MMTCE = 330 gal x 3.7854 l/gal x 1.7 kg/l x 9,000 x (12 C/44 CO₂)/10⁹ kg/MMT.

of HTF use in cooling, testing and soldering; the quantities of HTFs used and lost via evaporation from each use; whether HTFs have high or low GWPs (and what that value is²²); and what the values for fluid densities of the HTFs should be. The estimates in Table 4 are those associated with a specific single fab—a large product fab—a proxy for facilitating comparisons of fab-infrastructure emissions from high-GWP materials rather than inter-fab emissions of high-GWP emissions. The estimates of emissions in Table 4 represent the emissions during IC manufacture (e.g. from etching, chamber cleaning, chillers, and testing provided testing is done at the fab) as well as the emissions *associated* with IC and product manufacture (e.g., testing and VPR soldering when both are outsourced). Finally, the estimates were developed using a single density (1.7 kg/l) and single GWP (9000) to convert volumes of liquids to MMTCE units. The 1.7 kg/l value could be approximately 10 percent lower or 6 percent higher. In addition, liquid PFCs can have higher or lower GWPs, from as low as 300 to as high as 11,000 (T&T, 2001).

The column labeled Estimate 1 denotes the low-end of the range for VPR soldering, while the column labeled Estimate 2 reflects the higher end of the range. However, both estimates assume all ICs are mounted using VPR soldering.

As indicated in Table 4, approximately 90 percent (87 – 91 percent) of all emissions *associated* with electronics manufacturing occur during IC manufacture—before packaging and surface mounting in products and, perhaps, before testing. This share of all emissions is the sum of emissions from both gaseous and liquid PFC use, during IC manufacture, tool cooling, and possibly testing. In addition, it should be recalled that some testing is outsourced, so that, even if liquid-liquid shock testing is employed and included in T&T's estimate, those emissions may not always occur at the IC fab.

The second observation about the estimates in Table 4 is that emissions from liquid-liquid shock testing (0.0016 MMTCE) appear relatively small (<5 percent of the total), regardless of where they occur (i.e., whether they occur during IC manufacture or elsewhere during testing). Furthermore, if only air-air shock testing is performed, emissions of high-GWP from testing would be nil. Equally important, however, is the effect on this estimate of emissions of using alternative sampling rates. For liquid-liquid

²² In choosing a specific value for a GWP, for example, is it taken from the IPCC Second Assessment or Third Assessment Report?

TST, emissions are directly proportional to sampling rate, which was taken as 0.1 percent for the estimate (0.0016 MMTCE) in Table 4. The only support for this sampling rate was its consistency with expected annual economic value of fluid losses specified by a TST equipment manufacturer. If there were no other changes when making this estimate, except that the sampling rate were assumed to be 0.2 percent (twice the 0.1 percent estimate), the emissions would be 0.0032 MMTCE, twice the estimate in Table 4. However, as that sampling rate increases, fluid replacement costs also increase, which at some sampling rate would limit the use of liquid-liquid TST in favor of air-air TST.

The final observation about the entries in Table 4 applies to VPR soldering. At approximately 10 percent of total emissions, it is notable. However, the evidence for the extent of VPR soldering for surface mounting devices is conflicting and perhaps changing. More than one report suggested that VPR soldering technology was passé. Reports promoted the virtues of convection ovens, which avoid the high cost of PFC liquid replacement, provide high throughput and have much less waste disposal (except for lost heat associated with convection ovens). However, other reports promoted the virtues of VPR soldering (especially for lead-free soldering), which is emerging rapidly as the required method for surface-mounting devices. Thus, it could be argued that PFC emissions from VPR soldering might increase.

6.0 DISTRIBUTION OF SOURCES

The initial research suggests a fragmented, dynamic and global distribution of sources (i.e., users) of liquid PFCs in the electronic sector. Three segments of this sector—semiconductor manufacturers, electronic product manufacturers and electronic manufacture service (EMS) providers—would appear to account for most if not all of the sources of emissions from using liquid PFCs.

Figure 2 schematically depicts the relationship among these three segments. The figure is intended to illustrate emission source boundaries; circle sizes qualitatively illustrate relative sizes of emissions from the sectors.

The outer circle in Figure 2 denotes the entire electronics sector, which would include military contractors and system integrators; the next largest circle (within the outer circle) denotes fully vertically integrated companies, i.e., companies, like IBM, Motorola, Sony, Sharp, Hitachi and Toshiba, for example, who manufacture ICs—and in doing so use liquid PFC coolants—as well as test and assemble

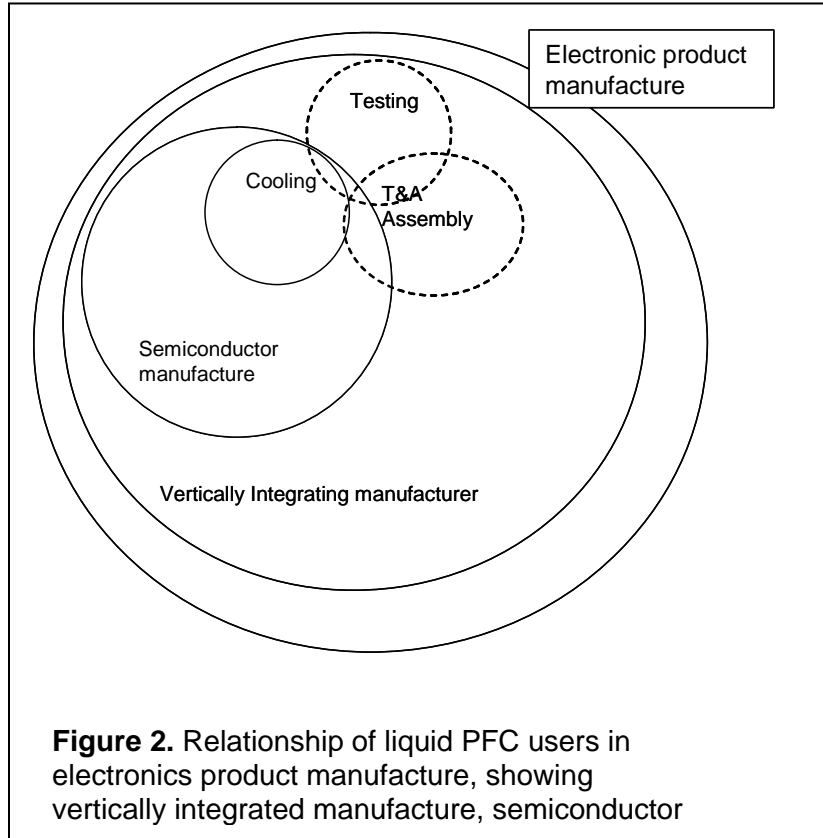


Figure 2. Relationship of liquid PFC users in electronics product manufacture, showing vertically integrated manufacture, semiconductor

those and merchant ICs into commercial products, which may also use liquid PFCs depending on the testing method and surface mounting technology. Within that circle are the semiconductor manufacturers (including foundries) which manufacture ICs (and also use liquid PFC coolants) but which may either perform all testing and assembly or subcontract portions to EMS providers, depicted by the dashed circles.

Figure 2 shows EMS providers as performing test or assembly services for vertically integrated manufacturers and semiconductor manufacturers or as providing both test and assembly services to these manufacturers, which is denoted by T&A where the dashed circles overlap. Finally, also illustrated in Figure 2 by the overlapping cooling and testing segments, is the use of liquid PFC coolants in test equipment. Not shown in Figure 2 are fabless companies; either IC foundries or EMS providers perform testing and assembly services for fabless companies.

There are many users of liquid PFCs. As previously described there are many technologies used in testing and assembly that do not use liquid PFCs, and no

information was obtained during this initial research that offered insights of their historical, current or projected use compared to those that use liquid PFCs. In seeking this information, some searches were made at websites of three trade associations that represent semiconductor manufacturing industry: Semiconductor Equipment Materials International (SEMI, www.semi.org), MicroElectronic Packaging and Test Engineering Council (MEPTEC, www.meptec.org), and Surface Mount Technology Association (SMTA, www.smta.org). SEMI, with its 2200 members represents the entire global semiconductor industry. MEPTEC and SMTA are smaller entities that aim exclusively at test and assembly. MEPTEC, a 25-year old association with 350 members (which includes many major semiconductor manufacturers), aims exclusively at advancing IC assembly and testing technologies. SMTA, a 20-year old association with 535 members (which includes a few relatively small semiconductor manufacturers) aims exclusively at surface mount technologies.

This fragmented picture of electronics sector is also dynamic. While industry reports often describe the accelerating trend toward more foundries and fabless companies, there are fewer reports about the increasing practice of outsourcing both testing and assembly to EMS providers. Three companies appear to have approximately 40 percent of this global market, ASE Group, Amkor Technologies, Inc. and STATS ChipPac (a recent merger between STATS, of Singapore, and ChipPac of Chandler, AZ) (Khadpe, 2004). Seven of the 10 largest companies have headquarters in Taiwan, Singapore and Malaysia (Khadpe, 2004). In 2003, for example, the share of the outsourced semiconductor assembly and test (OSAT) market associated with IDMs accounted for revenues of \$6.5 billion (or approximately 25 percent of IDM assembly and test expenses). By 2007, those revenues are projected to double to \$13 billion, which would then account for 30 percent of IDM assembly and test expenses and which represents an annual compound average growth rate of 20 percent, almost 3 times the corresponding growth rate of the semiconductor market. During this same period, the total OSAT market is projected to grow from \$26 billion in 2003 to \$43 billion in 2007 (see www.amkor.com).

Despite this fragmented and changing usage of liquid PFCs, it appears that, for the next few years, the semiconductor industry will remain a major source of emissions. The remainder of this section addresses the global distribution of semiconductor fabs that likely use liquid PFCs as coolants in TCUs and in IC testing and assembly.

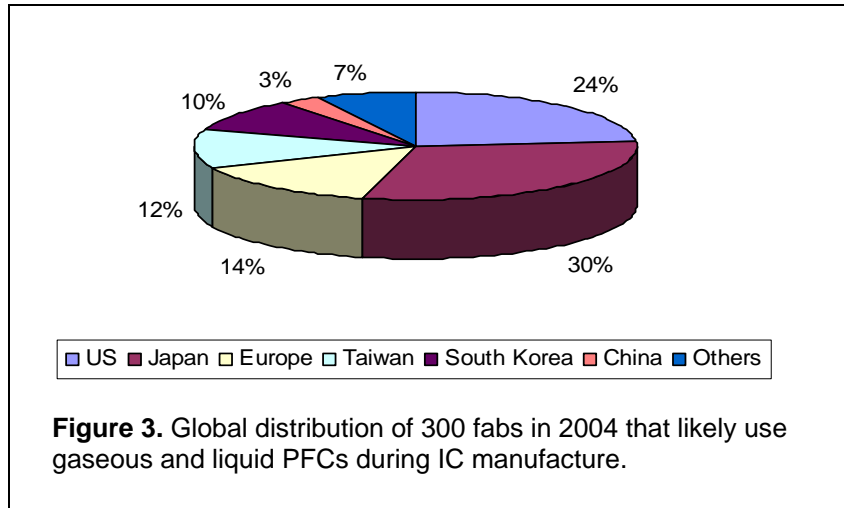


Figure 3. Global distribution of 300 fabs in 2004 that likely use gaseous and liquid PFCs during IC manufacture.

According to the January 2004 Edition of

SEMI's World Fab Watch, approximately 380 of 410 production fabs worldwide use gaseous PFCs.²³ Of the 380, approximately 300 fabs in 2004 are likely to use process technologies that employ TCUs during IC manufacture.^{24,25} Figure 3 shows the global distribution of those

300 fabs. The capacities of this population of 300 production fabs span approximately 300 – 70,000 wafer (200 mm equivalent) starts per month. Figure 4 shows the capacity distribution of these 300 fabs. Note

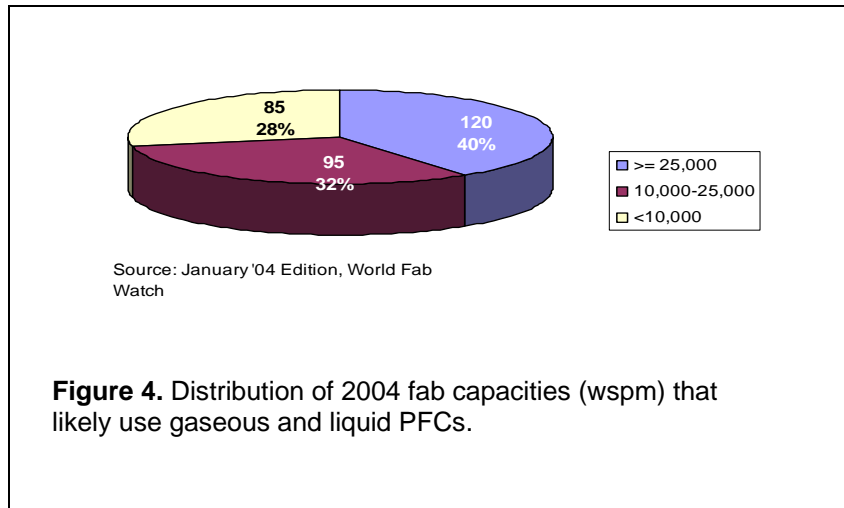


Figure 4. Distribution of 2004 fab capacities (wspm) that likely use gaseous and liquid PFCs.

that this distribution of capacities shows that 40 percent of the 300 production fabs are large. The distribution shown in Figure 4 together with the information in Table 4 can be used to estimate, roughly, global PFC emissions for 2004—an estimate that includes

²³ The 410 fabs include production fabs in operation in 2004 that use silicon wafers and ICs fabricated with feature sizes $\leq 1 \mu\text{m}$.

²⁴ The 300 fabs are those fabricating ICs with feature sizes $\leq 0.5 \mu\text{m}$, the technology node when TCUs began using liquid PFC coolants.

²⁵ In this analysis fabs that do not use gaseous PFCs are excluded because it is reasonably assumed that such fabs would use water/glycol TCUs rather than TCUs with liquid PFC HTFs.

gaseous and liquid PFC use during IC manufacture. This rough global estimate starts with 0.05 MMTCE from Table 4 (rounded to one significant figure to reflect the roughness of these estimates), the total PFC emissions during manufacture from a large fab. Assuming 0.05 MMTCE is the *average* total emissions for the 120 large fabs in Figure 4 gives 6 MMTCE ($=0.05 \times 120$) for the global emissions from this group of high-volume fabs. The average capacity of the medium size fab is approximately 15,000 wspm (200 mm) or, if emissions are assumed to be proportional to fab size, 0.025 MMTCE per fab. This group of 95 fabs, therefore, is estimated to contribute 2.4 MMTCE to the global total. The remaining group of small fabs contributes 0.6 MMTCE to the world total ($=0.007 \text{ MMTCE/fab} \times 85 \text{ fabs}$, where 0.007 MMTCE is emissions of the average size fab [4,000 wafer starts per month, wspm] in this group of small fabs). Thus, in 2004, the total global (gaseous plus liquid) PFC emissions from semiconductor manufacturing are estimated roughly at 9 MMTCE.²⁶

The next section examines alternative methods for estimating emissions from using liquid PFCs.

7.0 OPTIONS FOR ESTIMATING EMISSIONS FROM USING LIQUID PFCs IN ELECTRONICS MANUFACTURING

The preliminary research identified three alternative methods for estimating annual emissions from liquid PFC use. The first method relies on the share of total emissions—17 percent on an MMTCE basis—first presented by T&T (2001) and apparently similar to the corresponding share estimated from reported emissions by Seiko Epson and Mitsubishi. The second method uses T&T's estimate of 500 gallons of liquid PFC lost for their typical high-volume production fab, which could be scaled to account for varying fab sizes. The third method relies on manufacturers to report estimates of evaporative losses of liquid PFCs. The virtues of each method are presented in the remainder of this section.

7.1 Method 1: 17 Percent of all PFC Emissions Originate from Liquid PFC Losses

²⁶ An independently developed and arguably more precise estimate of global emissions is provided by PEVM for 2004: 8.4 MMTCE, which only includes uncontrolled gaseous PFC emissions. Thus, it appears that 0.6 MMTCE (or 7 percent = $0.6/9$ of the total) might be attributed to using liquid PFCs.

As discussed in Section 5 and shown in Table 3, emissions due to uses of liquid PFCs contribute approximately 17 percent to total PFC emissions (from both liquid and gaseous PFC usage). Using the 17 percent is simple, but unreliable. For the method to be reliable, this (or any) fraction must remain constant over time and constant with capacity. As shown by T&T (2001) the share not only cannot be assumed constant but is also increasing as semiconductor manufacturers implement measures to reduce emissions from using gaseous PFCs. The changing fraction is also evident in reports of Seiko Epson and Mitsubishi (cf. Table 3). In addition, as shown at the end of the previous section, evidence indicates the share decreases as fab capacity decreases (see footnote 27). Finally, even if these reasons could be overlooked, this method could not account for using alternative gaseous or liquid PFCs, which would likely have GWPs that differ with those reflected in the estimated 17 percent.

7.2 Method 2—500 Gallons Is Annual Loss per Fab, Across All Fab Sizes

The second method—assuming 500 gallons/fab for the loss across all fabs—while also simple and capable of accounting for changing values for GWPs, has serious limitations. While this 500 gal/year estimate for a 1999-2000 vintage fab is comparable to the published figures for Japanese semiconductor manufacturers, it is unreasonable to assume the losses for medium and small fabs would be the same.²⁷ To overcome this limitation, some method of scaling the 500 gallons figure is required. Second, even if some acceptable method of scaling were developed, the figure would likely not remain constant over time. As T&T suggest, the 500 gallons amount was probably considerably larger in the late 1990s, when semiconductor manufacturers failed to initially appreciate the propensity of liquid PFCs to leak (because of their very low surface tension) when used simply as drop-in substitutes for water/glycol coolants.

7.3 Method 3—Estimating Fab Specific Annual Losses Of Liquid PFCs

The third method is methodologically simple and reasonably relies on manufacturers to report annual losses. Companies representing approximately 70 percent of global semiconductor manufacturing capacity already estimate and report annual emissions of

²² Taking, for example, the estimate 4.8×10^4 Mtons for emissions from liquid PFCs for all of Seiko Epson for 1998 equates to 1,000 gallons lost (using the properties of C_6F_{14} , GWP of 7400 [SAR] and density of 1.7 kg/l). Because Seiko Epson operated two large fabs during this period, T&T's estimate of 500 gals/yr for one fab of comparable size and vintage is remarkable.

gaseous PFCs during IC manufacture. In this method, annual losses are calculated using the formula, for each liquid PFC used,

$$\begin{aligned} \text{Annual Loss (gallons)} &= \text{Annual emissions} \\ &= \text{“Top-off” of TCUs, testing and assembly equipment} + \text{losses from retired} \\ &\quad \text{equipment} - \text{on site disposal from retired equipment} \end{aligned}$$

Mathematically, this can be written as mass of emissions as a function of PFC quantities,

$$\text{PFC}_i \text{ (kg)} = \rho_i \{I_{i,t-1}(l) + P_{it}(l) + C_{it}(l) - N_{it}(l) - I_{it}(l) - D_{it}(l)\}$$

where

- ρ_i = density of liquid PFC_i, in kg/l, which is available from suppliers
- $I_{i,t-1}(l)$ = the inventory of liquid PFC_i at the end of the previous period in containers
- $P_{it}(l)$ = purchases of liquid PFC_i during the period,
- $C_{it}(l)$ = nameplate capacity of retired equipment
- $N_{it}(l)$ = quantity of liquid PFC_i for filling new equipment,
- $I_{it}(l)$ = inventory of liquid PFC_i at the end of the period in containers, and
- $D_{it}(l)$ = amount of PFC_i disposed from retired equipment during the period.

This formula is methodologically rigorous under the assumption that it accurately reflects the industry’s practice for managing its stores and uses of liquid PFC HTFs. It should be noted that 3M has a policy of cost-free pickup and return (to 3M) of used high-GWP HTFs in the U. S. provided quantities for return equal at least 30 gallons (see www.3m.com/fluids). Thus, in practice disposal is likely unimportant. In addition, to the extent material from decommissioned equipment is suitable for new equipment, recycling may be important. Tracking emissions in this manner is unlikely burdensome because manufacturers likely carefully track liquid PFC purchases and inventory as well as minimize extraneous losses due to the high cost of these liquids and semiconductor manufacturers’ practice of rigorous cost control.²⁹

An uncertainty with any method is the choice for GWP. This initial research indicates only 3M (which used accepted IPCC methodologies for estimating emissions) has

²⁹ This initial research did not reveal any pick-up and return policy offered by Solvay Solexis in Europe, the headquarters’ location or in the United States.

estimated GWPs for some of its Fluorinert and HFE (hydrofluoroether) fluids. However, this initial research did not identify the procedure 3M follows to estimate GWPs. In several instances (see T&T, for example), 3M suggests that users follow U. S. EPA's "recommendation" of using the GWP for C₆F₁₄ when no other value is available. However, the reference 3M cites for the source of this "recommendation" contains no explicit recommendation. In a footnote to Table 3-33 of the EPA, **Inventory of Greenhouse Gas Emissions and Sinks: 1990-2000** is a note that indicates "for estimating purposes, the GWP value used for [a diverse collection of PFC/PFPEs for solvent applications] was based on C₆F₁₄" (EPA, 2002). It should also be mentioned that the GWP for C₆F₁₄ from the Second Assessment Report is 7400 compared to the higher value, 9000, provided in the Third Assessment Report.

8.0 PROPOSED ADDITIONAL RESEARCH

This section proposes and summarizes additional work aimed at clarifying the

- Distribution of users of liquid PFC HTFs in the electronic sector
- Proportion of technologies that use liquid PFCs (and trends in those proportions) and
- Modes and amounts of emissions from liquid PFC uses.

This additional work should provide robust knowledge on which to base improved numerical estimates (with less uncertainty) of the contribution of liquid PFC emissions from the electronic sector.

The lack of readily available past and current estimates on annual, global quantities associated with liquid PFC HTF use in the electronic sector frustrates efforts to compare that use to similar uses in other sectors or different uses altogether. For example, chillers are prevalent in the manufacture of pharmaceuticals but this initial research could not address the extent to which liquid PFC HTFs might be used. In addition, there are direct medical applications of liquid PFCs in which all of the PFCs are lost to the atmosphere. Knowledge of the share of liquid PFCs use in the electronic sector would help resolve these uncertainties.

The lack of information about global use of liquid PFCs suggests that the uses may be too small— especially compared to quantities of other specialty chemicals used in the

electronics sector—to attract the interest of industry and market analysts.³⁰ However, the high cost of liquid PFCs indicates these are high-value chemicals. Their unique physical and chemical properties, together with 3M and Solvay Solexis' recent efforts to find and market low-GWP substitutes, suggests the uses and sales of liquid PFCs are sufficiently important to the future business of each enterprise to attract investment.

Much of the analysis in this report about the magnitude of emissions from liquid PFC use rests on T&T's estimate that the annual loss from a typical large high-production fab is 500 gallons of liquid PFC, which has the properties (density and GWP) of C₆F₁₄. The only corroboration of 3M's 500 gallon estimate comes from comparing that quantity, expressed as a fraction of total emissions from a 1999-2000 vintage typical high-volume production fab, with three other estimates: one from AMD global operations and two from Japanese electronic manufacturers. In the case of the estimates published by the Japanese manufacturers, the comparison of absolute quantities is encouraging though still speculative since they reflect enterprise totals rather than fab-specific quantities. Hence, the veracity and robustness of T&T's estimate warrants further investigation.

Further work also seems warranted regarding the share of liquid PFCs (and low-GWP substitutes) used for cooling, TST, and reflow soldering. As indicated previously, claims over the benefits of alternative methods are conflicting. This confusion is expected given that equipment manufacturers and material suppliers made the claims. While it seems intuitive that, in light of the high unit cost of liquid PFC, users might seek alternatives to using liquid PFCs, it has been and is the practice of the electronic sector to maximize throughput provided key technical requirements are achieved even if the cost of a specific item is relatively high.³¹ However, during periods when demand is low,

³⁰ Consider for example the likely largest current buyer of liquid PFCs, IC equipment manufacturers. Use T&T's estimate of 500 gallons/yr for replacement. Then assume 10 new fab/year being built (which seems generous at \$2-3 billion each and global capital expenditures for all new and existing fabs at \$40 – 50 billion/year), with each having 290 tools that use liquid PFCs (Figure 3, this report) at 25 gal/tool, on average. Add replacement and new sales. The result is an annual global volume of roughly 2.5 million pounds of liquid PFCs. These 2.5 million pounds can be compared to annual global NF₃ supply of approximately 14 million pounds of NF₃ in 2004, which is one of 7 gases used in IC and LCD manufacture. Of course, this estimate of 2.5 million pounds liquid PFC consumption neglects other uses, which, even if they were comparable to or a small multiple of the use by IC manufacturers, would result in a higher estimate for the liquid PFC volumes but still small compared to annual volumes of other specialty chemicals.

³¹ The use of NF₃ in chamber cleaning is a noteworthy example of industry thinking. Initially, the cost of NF₃ exceeded the cost of the dominant alternative (C₂F₆) by roughly 20-fold. However, the

throughput matters less than costs, so electronic manufacturers employ a mix of alternatives to hedge economic and technological risks.

Finally, additional information about the annual losses of liquid PFCs during TST and VPR soldering is warranted. This review revealed not only wide variability—a factor of 10 in both TST and VPR soldering uses—but included claims that losses were being reduced through equipment redesigns as well as, in the case of VPR soldering, through the use of a secondary Fluorinert fluid.

benefits of NF_3 more than compensated for its much higher cost. Today, production volumes of NF_3 are approaching those of C_2F_6 .

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